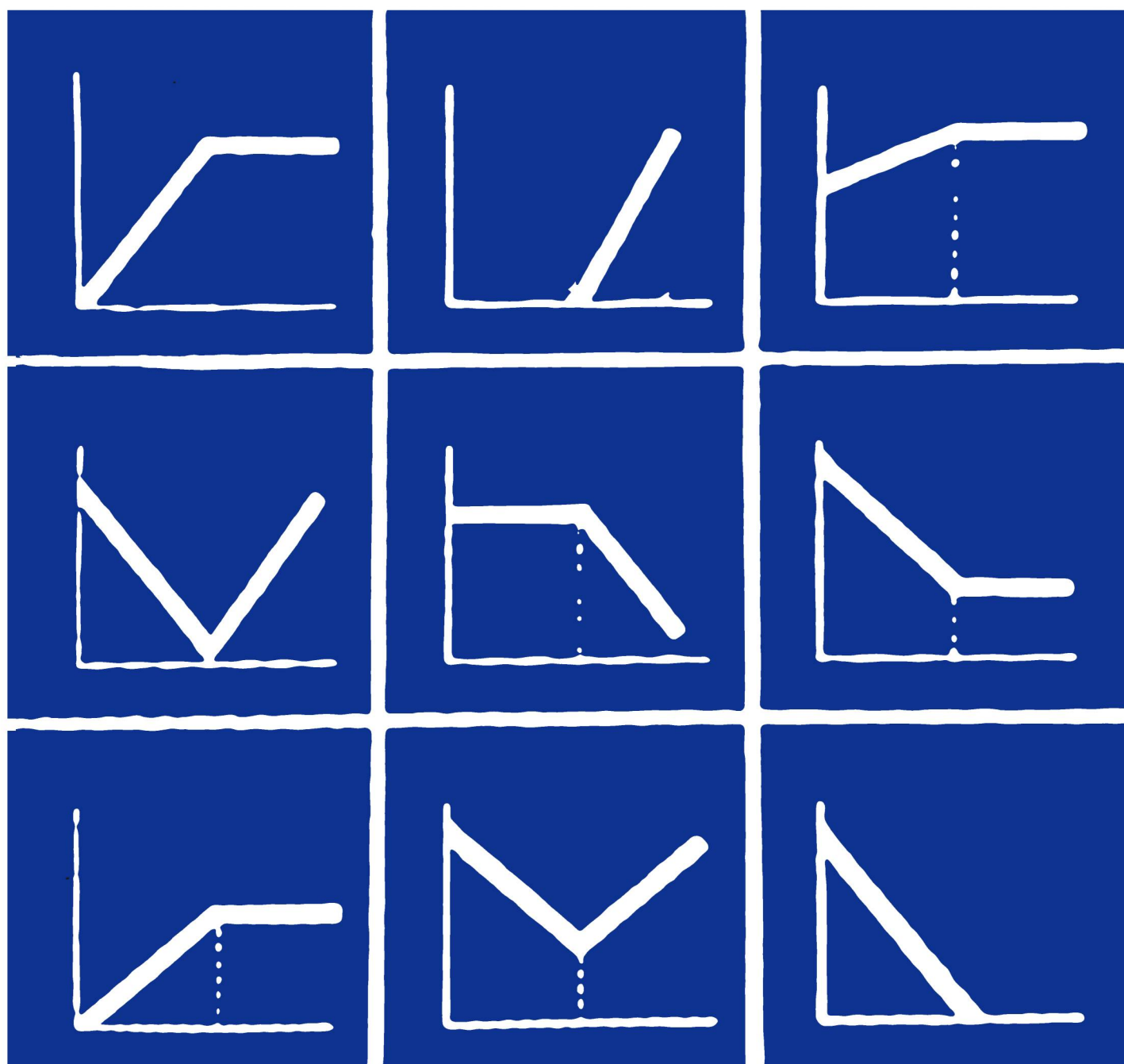


Problems in PHYSICOCHEMICAL METHODS of Analysis

Yu. Lyalikov, M. Bulatov, V. Bodyu, S. Krachun



Mir Publishers Moscow

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Ю. С. ЛЯЛИКОВ, М. И. БУЛАТОВ,
В. И. БОДЮ, С. В. КРАЧУН

ЗАДАЧНИК ПО ФИЗИКО-ХИМИЧЕСКИМ МЕТОДАМ АНАЛИЗА

ИЗДАТЕЛЬСТВО «ХИМИЯ»
МОСКВА

Yu. LYALIKOV, M. BULATOV,
V. BODYU, S. KRACHUN

PROBLEMS IN PHYSICOCHEMICAL METHODS OF ANALYSIS

Translated from the Russian
by
ARTAVAZ BEKNAZAROV

MIR PUBLISHERS MOSCOW

First published 1974
Second printing 1984

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PREFACE

Courses in physicochemical methods of analysis are included in curricula of numerous educational establishments. The problems however are given little emphasis in many textbooks and manuals. The authors of the present problem book have made their aim to fill up this gap and to set up problems in the principal methods of physicochemical analysis and methods of separating substances.

Since methods of programmed instruction have recently been introduced at higher school, each chapter of the book includes assignments for programmed questioning.

Most of the chapters consist of the following sections:

1. *Examples of problem-solving.*

2. *Multivariant problems.* This section covers problems involving simple single-type calculations based on a definite formula or law.

3. *Problems.* This section contains problems of three types: A, B, and C. Problems of type A are primarily intended for college students and workers in plant laboratories. Problems of type B are more complicated and are meant for students at universities and higher schools. And, finally, problems of type C, the solution of which requires the use of literature data, are designed for students at most advanced level, who wish to major in the field of physicochemical methods of analysis. In some of the problems of types B and C, physicochemical methods are used for determination of constants such as the solubility products, complex-formation constants.

4. *Assignments for programmed questioning.* This section contains programmed assignments based on four principles. In assignments compiled according to the *multiple-choice principle*, one must choose, among a number of answers to a given question, the correct ones. In some cases, of

5 answers only one is correct, in others, among 7 to 9 answers 3 or 4 are correct, though expressed in different form. In assignments based on the *linear principle*, one group contains questions and the other gives alternately one and occasionally several answers to these questions. In assignments based on the *principle of variants*, the question placed in the first group is provided with two answers supplementing each other in two other groups. In assignments set up according to the *detailed-answer principle*, to each question there correspond two rows of answers, of which one is correct and the others (4 answers) are wrong. The second row of answers supplement or detail the answers given in the first row. This is a complex type of programmed questioning.

In certain cases assignments are included for teaching machines.

For the student to acquire the skill of using reference literature, the authors considered it expedient, in a number of problems marked with one asterisk, to leave out certain information (the densities of solutions, oxidation-reduction potentials, electrical conductances, etc.). The handbook that is recommended for use as a data source is *Handbook of Chemistry* by N. A. Lange, McGraw-Hill Book Company, 1961. The cases where other handbooks are to be resorted to are specified in the directions to a particular problem.

For more sophisticated problems marked with double asterisks, primarily those of types B and C, directions are provided at the end of the book, indicating the way a given problem is to be solved. Naturally, the student should not resort immediately to these directions.

A list of books is supplied at the end of this book, which are recommended for study and recapitulation of the theoretical foundations of physicochemical methods.

The authors wish to express their deep gratitude to the referees of the book—Professors K. N. Mochalov and Yu. A. Klyachko for valuable suggestions and advice, which contributed to the improvement of the manuscript.

This problem book is the first attempt at compiling a text of this kind, and the authors will accept with gratitude all remarks and suggestions, which, we hope, will help improve the book.

The authors

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Mathematical Treatment of Analytical Results

Two techniques are used for treatment of analytical results: the statistical method and the method of approximate calculations. The former is employed in Examples 1 and 2, Multivariant Problem 1 and Problems 1-4, 13, 14, 22-25; the latter is used in the remaining problems.

Brief theoretical information on the mathematical treatment of the results of analysis may be found in *Physicochemical Methods of Analysis*, a textbook, written by Yu. S. Lyalikov (this book has been published in English by Mir Publishers, Moscow, USSR, 1968, under *Physicochemical Analysis*). More detailed information may be found in the books listed at the end of this book.

Symbols and Terms Used

Statistical Methods

The *measured value* is the observed value of the quantity being measured.

The *result* is the final value of the measured quantity, obtained after all auxiliary processes and operations.

An *individual sample value* is the measured value used for statistical treatment. It is designated by the symbol x .

A *sample array* is a certain number of individual values which are equivalent to one another from the standpoint of statistics (x_1, x_2, x_3, \dots).

The *mean value* is the sum of a set of individual values divided by their number in the sample array. The symbol is \bar{x} .

The *reliability* of the mean is defined as the difference between it and the true value of the magnitude measured.

The *deviation* is the difference between an individual value and the mean of the sample array to which it belongs. The symbol is d .

The *range* is the difference between the highest and the lowest measured value in the array. It is designated as $R = x_{\max} - x_{\min}$.

The *standard deviation* is found by extracting the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from the mean by one less than the number of determinations made:

$$\bar{s} = \sqrt{\frac{\sum d^2}{n-1}}$$

The *standard deviation of the mean* is the standard deviation divided by the square root of the total number of determinations made. The symbol is $\sigma_{\bar{x}} = \bar{s}/\sqrt{n}$. This term is missing in the IUPAC recommendations, but it is widely used.

Dispersion or *spread* is the square of the standard deviation. It is denoted by $V = \sum d^2/(n-1)$.

The *relative standard deviation* is the standard deviation of the mean divided by the mean of the sample array. It is defined as follows: $s_{\text{rel}} = \sigma/\bar{x}$ or, in per cent, $s_{\text{rel}} = (\sigma/\bar{x}) 100$.

The *sample size* is the total number of individual values in a sample array. It is denoted by n .

The *error* is the difference between an actual measurement and the true value of the magnitude measured.

The *percentage error* is the error expressed in per cent of the true value.

The *confidence level* is designated by α .

The coefficient of *standardized deviations* (*Student's coefficient*) is denoted by $t_{\alpha, k}$.

The number of *degrees of freedom* is one less than the number of determinations (individual values) in a sample array. It is designated as $k = n - 1$.

The *accuracy* of a single measurement at a chosen confidence level is the product of the standard deviation by the standardized deviation coefficient divided by the

square root of the number of determinations (sample size):

$$\varepsilon_{\alpha} = \frac{\bar{st}_{\alpha, h}}{\sqrt{n}} = \sigma t_{\alpha, h}$$

The *relative error* of a direct determination is the ratio of the accuracy of a measurement to the mean, expressed in per cent: $\Delta = (\varepsilon_{\alpha}/\bar{x}) 100$.

The *confidence interval* (*confidence limits*) of the quantity being determined is $\bar{x} \pm \varepsilon_{\alpha}$.

The criterion F is equal to V_1/V_2 .

The criterion Q is equal to $(x_1 - x_2)/R$ (where $x_1 - x_2$ is the difference of the neighbouring measured values, of which one is doubtful).

The Method of Approximate Calculations

The absolute error of the quantities measured is designated as f_x and f_y .

The relative error of measured values is given by

$$\delta_{x(y)} = f_{x(y)}/x(y) \cdot 100$$

To relieve the reader of the burden of searching for the necessary table data we give here Student's coefficients and values of the criteria F and Q (given for the most frequently used 0.95 or 95% confidence limits), which will be needed for solution of problems.

TABLE 1

| Number of experiments in a series | Number of series of experiments | | | | | | |
|-----------------------------------|---------------------------------|-------|-------|-------|-------|-------|-------|
| | 2 | 3 | 4 | 5 | 6 | 8 | 10 |
| 2 | 19.00 | 19.16 | 19.25 | 19.30 | 19.33 | 19.37 | 19.39 |
| 3 | 9.55 | 9.28 | 9.12 | 9.01 | 8.94 | 8.84 | 8.78 |
| 4 | 6.94 | 6.59 | 6.39 | 6.26 | 6.16 | 6.04 | 5.96 |
| 5 | 5.79 | 5.41 | 5.19 | 5.05 | 4.95 | 4.82 | 4.74 |
| 6 | 5.14 | 4.76 | 4.53 | 4.39 | 4.28 | 4.15 | 4.06 |
| 8 | 4.46 | 4.07 | 3.84 | 3.69 | 3.58 | 3.44 | 3.34 |
| 10 | 4.10 | 3.71 | 3.48 | 3.33 | 3.22 | 3.07 | 2.97 |

The coefficients of standardized deviations, or Student's coefficients, are as follows:

| | | | | | | | | | | | | | | | |
|----------------|----|---------------|---|---|---|---|---|---|---|---|--------|-------|-------|-------|-------|
| k | . | . | . | . | . | . | . | . | . | . | 1 | 2 | 3 | 4 | 5 |
| $t_{\alpha,k}$ | at | $\alpha=0.95$ | . | . | . | . | . | . | . | . | 12.706 | 4.303 | 3.182 | 2.776 | 2.571 |
| k | . | . | . | . | . | . | . | . | . | . | 6 | 7 | 8 | 9 | 10 |
| $t_{\alpha,k}$ | at | $\alpha=0.95$ | . | . | . | . | . | . | . | . | 2.447 | 2.365 | 2.306 | 2.262 | 2.228 |

The values of the criterion F are given in Table 1.

The values of the criterion Q are as follows:

| | | | | | | | | | | | | | | |
|----------------------|---|---|---|---|---|---|------|------|------|------|------|------|------|------|
| n | . | . | . | . | . | . | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Q at $\alpha=0.95$ | . | . | . | . | . | . | 0.94 | 0.77 | 0.64 | 0.56 | 0.51 | 0.48 | 0.44 | 0.42 |

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. In determining molybdenum in ore in duplicate samples the following amounts of MoO_3 were found in weighed portions of 0.5000 g: 0.02851, 0.02856, 0.02873, 0.02852, 0.02831, 0.02856, 0.02851, 0.02853, 0.02855, 0.02850.

Treat these data according to mathematical statistics and determine the percentage content of molybdenum in the ore.

Solution. Before starting the statistical treatment of the experimental data a check is to be done to see whether there are values which differ sharply due to crude errors. If there are such values, you are to exclude them from the series to be statistically treated. To accomplish this, arrange the experimental data in increasing order: 0.02831, 0.02850, 0.02851, 0.02851, 0.02852, 0.02853, 0.02855, 0.02856, 0.02856, 0.02873.

Suppose that the values 0.02831 and 0.02873 are unreliable. Calculate the criteria Q for them:

$$Q_1 = \frac{0.02850 - 0.02831}{0.02873 - 0.02831} = 0.45$$

$$Q_{10} = \frac{0.02873 - 0.02856}{0.02873 - 0.02831} = 0.41$$

For $\alpha = 0.95$ and $n = 10$ the tabulated value of Q is equal to 0.42. Since Q_t is less or almost equal to Q_1 and Q_{10} , the two values x_1 and x_{10} are unreliable and are therefore dropped. We write down the remaining values in tabular

form (see Table 2) and find the arithmetic mean of the content of MoO_3 , \bar{g} , the standard deviation \bar{s} and the accuracy of the determination ε_α .

$$\begin{aligned}\varepsilon_{0.95} &= \frac{t_{\alpha, h\bar{s}}}{\sqrt{n}} = \frac{2.37 \times 2.39 \times 10^{-5}}{2.82} = \\ &= 1.98 \times 10^{-5} \text{ g} \approx 2 \times 10^{-5} \text{ g}\end{aligned}$$

TABLE 2

| g | \bar{g} | $(g - \bar{g}) \cdot 10^5$ | $(g - \bar{g})^2 \cdot 10^{10}$ | \bar{s} |
|---------|-----------|----------------------------|---------------------------------|--|
| 0.02850 | 0.02853 | -3 | 9 | $\sqrt{\frac{40 \times 10^{-10}}{8-1}} =$ $= \sqrt{5.7 \times 10^{-10}} =$ $= 2.39 \times 10^{-5}$ |
| 0.02851 | | -2 | 4 | |
| 0.02851 | | -2 | 4 | |
| 0.02852 | | -1 | 1 | |
| 0.02853 | | 0 | 0 | |
| 0.02855 | | +2 | 4 | |
| 0.02856 | | +3 | 9 | |
| 0.02856 | | +3 | 9 | |
| | | | 40 | |

Estimating the presence of crude errors from the criteria $\varepsilon_\alpha \sqrt{2}$ and $3\bar{s}/\sqrt{n}$, we obtain:

$$\begin{aligned}\frac{\bar{s}}{\sqrt{n}} &= \frac{2.39 \times 10^{-5}}{\sqrt{8}} = \frac{2.39 \times 10^{-5}}{2.82} = 8.5 \times 10^{-6} \\ 3 \frac{\bar{s}}{\sqrt{n}} &= 3 \times 8.5 \times 10^{-6} = 2.55 \times 10^{-5} \approx 3 \times 10^{-5}\end{aligned}$$

$$\varepsilon_{0.95} \sqrt{2} = 1.98 \times 10^{-5} \times 1.4 = 2.78 \times 10^{-5} \approx 3 \times 10^{-5}$$

As seen from Table 2, none of the deviations from the mean is outside the limits of the values found, which means that there are no crude errors in these measurements. The mean value of the quantity measured, which covers 95 per cent of all the measurements, is (0.02853 ± 0.00002) g of MoO_3 .

Using the conversion factor for changing MoO_3 to Mo, 0.6666, we find the percentage of molybdenum in the ore:

$$\frac{(0.02853 \pm 0.00002) 0.6666 \times 100}{0.5000} = (3.803 \pm 0.003) \text{ per cent}$$

Example 2. To determine the normality of a solution of HCl, three weighed portions of Na_2CO_3 were taken: 159.0, 174.9, and 190.8 mg (when the samples were weighed twice, the deviation did not exceed ± 0.1 mg). Each sample was dissolved in 25 ml of water. A 5-ml volume of each solution was taken for titration; therefore the volume of the acid used up was then multiplied by 5 for the volume of the whole sample to be taken into account. The following volumes of hydrochloric acid, in ml, were used for titration:

| | | | | | |
|-------|-----------|-------|-------|-------|-------|
| w_1 | | 15.10 | 15.15 | 15.07 | 15.05 |
| w_2 | | 16.60 | 16.65 | 16.65 | 16.55 |
| w_3 | | 18.10 | 18.15 | 18.07 | 18.05 |

Calculate the most probable value of the normality of the HCl solution and the accuracy and relative error of the determination for a confidence level of $\alpha = 0.95$.

Solution: We calculate for each series:

(1) the mean value of the volume

$$\bar{w}_i = \frac{\sum w_i}{n}$$

(2) the selective dispersion of the volumes

$$V_{w_i} = \frac{\sum (w - \bar{w}_i)^2}{n-1}$$

(3) the selective dispersion of the weights of the samples, which, after double weighing, will be equal for all the series:

$$V_{p_i} = \frac{\sum (p_i - \bar{p})^2}{n-1} = \frac{2 \times 10^{-2}}{2-1} = 2 \times 10^{-2} \text{ mg}$$

(4) the dispersion of the normality values

$$\begin{aligned} V_{N_i} &= \frac{\partial \left(\frac{p_i}{E_{\text{Na}_2\text{CO}_3} w_i} \right)^2}{\partial w_i} V_{w_i}^2 + \frac{\partial \left(\frac{p_i}{E_{\text{Na}_2\text{CO}_3} w_i} \right)^2}{\partial p_i} V_{p_i}^2 = \\ &= \frac{p_i^2 V_{w_i}^2}{53^2 w_i^4} + \frac{V_{p_i}^2}{53^2 w_i^2} \end{aligned}$$

All the calculation data can conveniently be collected in tabular form (see Table 3).

TABLE 3

| Series of ex- peri- ments | n_i | p_i , mg | \bar{w}_i , ml | $V w_i = \frac{\sum (w - \bar{w}_i)^2}{n - 1}$ | $N_i = \frac{p_i}{E \text{Na}_2\text{CO}_3 \bar{w}_i} \text{ g-eq/litre}$ | V_{N_i} |
|------------------------------------|-------|------------|------------------|--|---|---|
| 1 | 4 | 159.0 | 15.09 | $\frac{57 \times 10^{-4}}{3} = 1.9 \times 10^{-3}$ | $\frac{159.0}{53 \times 15.09} = 0.1988$ | $\frac{159^2 \times 1.9 \times 10^{-3}}{53^2 \times 15.09^4} + \frac{2 \times 10^{-2}}{53^2 \times 15.09^2} = 32.9 \times 10^{-8} + 3.1 \times 10^{-8} = 3.60 \times 10^{-7}$ |
| 2 | 4 | 174.9 | 16.59 | $\frac{69 \times 10^{-4}}{3} = 2.3 \times 10^{-3}$ | $\frac{174.90}{53 \times 16.59} = 0.1989$ | $\frac{174.9^2 \times 2.3 \times 10^{-3}}{53^2 \times 16.59^4} + \frac{2 \times 10^{-2}}{53^2 \times 16.59^2} = 33.0 \times 10^{-8} + 2.6 \times 10^{-8} = 3.56 \times 10^{-7}$ |
| 3 | 4 | 190.8 | 18.09 | $\frac{57 \times 10^{-4}}{3} = 1.9 \times 10^{-3}$ | $\frac{190.8}{53 \times 18.09} = 0.1991$ | $\frac{190.8^2 \times 1.9 \times 10^{-3}}{53^2 \times 18.09^4} + \frac{2 \times 10^{-2}}{53^2 \times 18.09^2} = 23.0 \times 10^{-8} + 2.2 \times 10^{-8} = 2.52 \times 10^{-7}$ |

To check the magnitude of the difference between the data of the whole set of experiments the criterion F is used:

$$F_{1-2} = \frac{V_{N_1}}{V_{N_2}} = \frac{3.60 \times 10^{-7}}{3.56 \times 10^{-7}} \approx 1$$

$$F_{1-3} = \frac{V_{N_1}}{V_{N_3}} = \frac{3.60 \times 10^{-7}}{2.52 \times 10^{-7}} = 1.43$$

$$F_{2-3} = \frac{V_{N_1}}{V_{N_3}} = \frac{3.56 \times 10^{-7}}{2.52 \times 10^{-7}} = 1.42$$

Treatment of Observation Results. The criterion F at $\alpha = 0.95$ and $n - 1 = 3$ is equal to 9.28 (see Table 1). Hence, there is no statistically significant difference between the data of all the series of experiments.

The mean value \bar{N} , the dispersion V_N and the accuracy ε_α are therefore calculated for the data of all the three series:

$$\begin{aligned} \bar{N} &= \frac{n_1 \bar{N}_1 + n_2 \bar{N}_2 + n_3 \bar{N}_3}{n_1 + n_2 + n_3} = \\ &= \frac{4 \times 0.1988 + 4 \times 0.1989 + 4 \times 0.1991}{4 + 4 + 4} = 0.1989 \text{ g-eq/litre} \\ V_N &= \frac{n_1 V_{N_1} + n_2 V_{N_2} + n_3 V_{N_3} + n_1 (\bar{N}_1 - \bar{N})^2 + n_2 (\bar{N}_2 - \bar{N})^2 + n_3 (\bar{N}_3 - \bar{N})^2}{n_1 + n_2 + n_3} = \\ &= \frac{4 \times 3.60 \times 10^{-7} + 4 \times 3.56 \times 10^{-7} + 4 \times 2.52 \times 10^{-7} +}{12} \\ &\quad + \frac{4 \times 1 \times 10^{-8} + 4 \times 4 \times 10^{-8}}{12} = \frac{4 \times 101.8 \times 10^{-8}}{12} = 3.40 \times 10^{-7} \end{aligned}$$

Having chosen the value of $t_{\alpha, k}$ at $\alpha = 0.95$ and $n_1 + n_2 + n_3 - 3$ degrees of freedom (2.26), we calculate the value of ε_α and the confidence interval for the value of N_{HCl} :

$$\begin{aligned} \varepsilon_\alpha &= t_{\alpha, k} \sqrt{\frac{V_N}{n_1 + n_2 + n_3}} = 2.26 \sqrt{\frac{3.40 \times 10^{-7}}{12}} = \\ &= 3.8 \times 10^{-4} \approx 4 \times 10^{-4} \text{ g-eq/litre} \end{aligned}$$

$$N_{\text{HCl}} = \bar{N} \pm \varepsilon_\alpha = 0.1989 \pm 0.0004 \text{ g-eq/litre}$$

The relative error of the determination is equal to

$$\Delta = \pm \frac{\varepsilon_\alpha}{\bar{N}} 100 = \pm \frac{4 \times 10^{-4} \times 100}{0.1989} = \pm 0.20 \text{ rel. per cent}$$

The solution of this problem can be simplified since the mean values of the normality of the HCl solution are very close to each other and $(\bar{N}_i - \bar{N}) < V_N$. Hence, the values of N_i may be regarded as the results of direct measurements; in this case

$$\bar{N} = \frac{1}{n} \sum N_i = \frac{1}{3} \sum \bar{N}_i = 0.1989 \text{ g-eq/litre}$$

$$V_N = \frac{\sum (\bar{N}_i - \bar{N})^2}{n-1} = \frac{5 \times 10^{-8}}{2} = 2.5 \times 10^{-8}$$

$t_{\alpha, k}$ at $\alpha = 0.95$ and $k = n - 1 = 2$ is equal to 4.3

$$\begin{aligned} \varepsilon_\alpha &= t_{\alpha, k} \cdot \frac{\bar{s}_N}{\sqrt{n}} = 4.3 \sqrt{\frac{2.5 \times 10^{-8}}{3}} = \\ &= 3.92 \times 10^{-4} \approx 4 \times 10^{-4} \text{ g-eq/litre} \end{aligned}$$

$$N_{\text{HCl}} = \bar{N} \pm \varepsilon_\alpha = 0.1989 \pm 0.0004 \text{ g-eq/litre}$$

$$\Delta = \pm \frac{\varepsilon_\alpha}{\bar{N}} \times 100 = \frac{4 \times 10^{-4}}{0.1989} \times 100 = 0.20 \text{ rel. per cent}$$

Example 3. The size of a grain of austenite, y , as a function of the heating temperature, t , is given by the equation

$$y = A \cdot 10^{-B/t}$$

What system of coordinates must be chosen for the relation between y and t to be expressed by a straight line?

Solution: Taking the logarithm of the above relation, we get:

$$\log y = \log A - \frac{B}{t}$$

Introducing new variables, $z = \log y$ and $u = 1/t$, we obtain the equation of a straight line:

$$z = \log A - Bu$$

Hence, the graph must be plotted by laying off $\log y$ along the ordinate and $1/t$ along the abscissa;

the graph will have the shape shown in Fig. 1.

Example 4. The equivalent electrical conductance λ (in

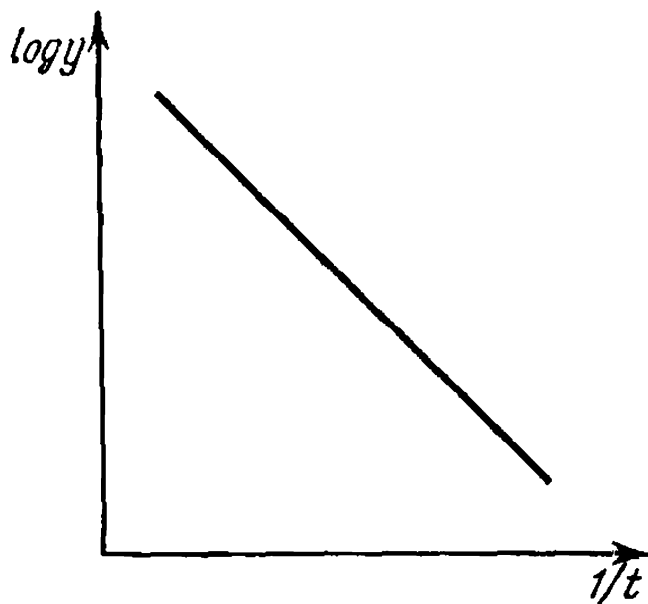


Figure 1

ohm⁻¹·g-eq⁻¹·cm²) of hydrochloric acid at different concentrations (in g-eq/litre) has the following values:

| | | | | | | |
|-----------|-------|-------|-------|-------|-------|-------|
| C | 0.001 | 0.005 | 0.010 | 0.020 | 0.050 | 0.100 |
| λ | 421 | 415 | 412 | 407 | 399 | 391 |

Derive a relation between C and λ of the type $\lambda = \lambda_{\infty} - k\sqrt[3]{C}$ by using the method of mean equations.

Solution: We calculate $\sqrt[3]{C}$ and break up all the data into two groups:

| I | | | II | | |
|-------------|-------|-----------------|-------------|-------|-----------------|
| λ_1 | C_1 | $\sqrt[3]{C_1}$ | λ_2 | C_2 | $\sqrt[3]{C_2}$ |
| 421 | 0.001 | 0.10 | 415 | 0.005 | 0.17 |
| 412 | 0.010 | 0.22 | 407 | 0.020 | 0.27 |
| 399 | 0.050 | 0.37 | 391 | 0.100 | 0.47 |
| <hr/> | | <hr/> | <hr/> | | <hr/> |
| 1232 | | 0.69 | 1213 | | 0.91 |

We set up two equations:

$$1232 = 3\lambda_{\infty} - k \times 0.69$$

$$1213 = 3\lambda_{\infty} - k \times 0.91$$

Solving these simultaneous equations, we obtain:

$$k = \frac{1232 - 1213}{0.91 - 0.69} = 86$$

$$\lambda_{\infty} = \frac{1232 + 86 \times 0.69}{3} = 431$$

The sought-for equation has thus the following form:

$$\lambda = 431 - 86\sqrt[3]{C}$$

Comparing the experimental data with the values of λ calculated from this equation, we obtain:

| | | | | | | |
|---|-------|-------|-------|-------|-------|-------|
| C | 0.001 | 0.005 | 0.010 | 0.020 | 0.050 | 0.100 |
| λ_{exp} | 421 | 415 | 412 | 407 | 399 | 391 |
| λ_{cal} | 423 | 417 | 412 | 408 | 399 | 391 |
| $\Delta\lambda = \lambda_{\text{cal}} - \lambda_{\text{exp}}$ | +2 | +2 | 0 | +1 | 0 | 0 |

The agreement between the values is satisfactory.

Example 5. Two quantities, x and y , are interrelated by an equation of the type

$$y^2 = A + \frac{B}{x}$$

Determine the coefficients A and B for this equation from the values of x and y given below:

| | | | | | | | | |
|-----|------|------|------|------|------|------|------|------|
| x | 1.54 | 0.80 | 0.48 | 0.36 | 0.29 | 0.24 | 0.21 | 0.20 |
| y | 3.3 | 4.1 | 4.7 | 5.0 | 5.6 | 5.9 | 6.0 | 6.6 |

Solution: Calculate the values of $1/x$ and y^2 :

| | | | | | | | | |
|-------|------|------|------|------|------|------|------|------|
| $1/x$ | 0.65 | 1.25 | 2.10 | 2.80 | 3.40 | 4.20 | 4.75 | 5.00 |
| y^2 | 11.0 | 16.8 | 22.2 | 25.0 | 31.4 | 34.8 | 36.0 | 43.6 |

On the basis of the calculated values of y^2 and $1/x$ we construct a graph (see Fig. 2).

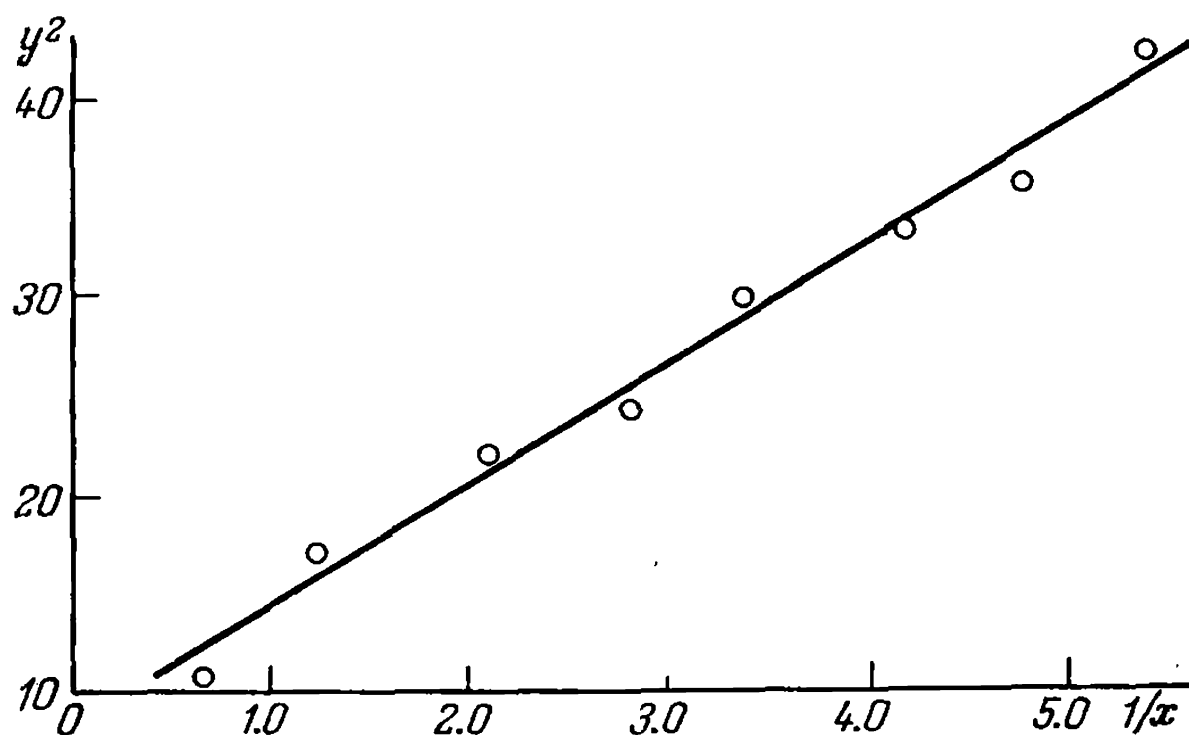


Figure 2

By applying the method of least squares we arrange the values of the indicated functions in tabular form (see Table 4).

Using the tabulated data, we find:

$$\left(\frac{1}{x}\right)^2 = (24.15)^2 = 580$$

TABLE 4

| y^2 | $1/x$ | $y^2(1/x)$ | $(1/x)^2$ | y^2 | $1/x$ | $y^2(1/x)$ | $(1/x)^2$ |
|-------|-------|------------|-----------|-------|-------|------------|-----------|
| 11.0 | 0.65 | 7.15 | 0.42 | 34.8 | 4.20 | 146.0 | 17.64 |
| 16.8 | 1.25 | 21.10 | 1.56 | 36.0 | 4.75 | 171.0 | 22.56 |
| 22.2 | 2.10 | 46.6 | 4.41 | 43.6 | 5.00 | 218.0 | 25.00 |
| 25.0 | 2.80 | 70.0 | 7.84 | | | | |
| 31.4 | 3.40 | 106.0 | 11.56 | 220.8 | 24.15 | 785.85 | 90.99 |

Now we determine the coefficients A and B , using the well-known equations:

$$\begin{aligned}
 A &= \frac{\sum \frac{1}{x} \sum \frac{1}{x} y^2 - \sum \left(\frac{1}{x}\right)^2 \sum y^2}{\left(\sum \frac{1}{x}\right)^2 - n \sum \left(\frac{1}{x}\right)^2} = \\
 &= \frac{24.15 \times 785.85 - 90.99 \times 220.8}{580 - 8 \times 90.99} = 7.9 \\
 B &= \frac{\sum \frac{1}{x} \sum y^2 - n \sum \frac{1}{x} y^2}{\left(\sum \frac{1}{x}\right)^2 - n \sum \left(\frac{1}{x}\right)^2} = \\
 &= \frac{24.15 \times 220.8 - 8 \times 785.85}{580 - 8 \times 90.99} = 6.5
 \end{aligned}$$

The equation now has the form

$$y^2 = 7.9 + \frac{6.5}{x}$$

We check the deduced equation by calculating y^2 and comparing the values obtained with experimental data (see Table 5).

The standard deviation is equal to

$$\bar{s} = \sqrt{\frac{14.12}{8-1}} = \sqrt{2.02} = 1.3$$

Thus, it is sufficient to measure the values of y^2 and y accurate to unity.

TABLE 5

| Experimental data | | Calculated from the equation | | |
|-------------------|----------------|------------------------------|-----------------|---------------------------------|
| 1/x | y ² | y ² | Δy ² | (Δy ²) ² |
| 0.65 | 11.0 | 9.6 | −1.4 | 1.96 |
| 1.25 | 16.8 | 15.7 | −1.1 | 1.21 |
| 2.10 | 22.2 | 21.5 | −0.7 | 0.49 |
| 2.80 | 25.1 | 26.1 | +1.0 | 1.00 |
| 3.40 | 30.8 | 30.0 | −0.8 | 0.64 |
| 4.20 | 34.1 | 35.2 | +0.9 | 0.81 |
| 4.75 | 36.0 | 38.4 | +2.4 | 5.76 |
| 5.25 | 43.2 | 41.7 | −1.5 | 2.25 |
| | | | | 14.12 |

2. MULTIVARIANT PROBLEMS

1. Calculate the values of x from the data presented in Table 6 and determine the absolute and relative errors of calculations.

2. Find the systems of coordinates in which the relations between x and y for the equations given are expressed by the following straight lines:

$$\text{I. } \frac{1}{y} = A + B^x$$

$$\text{V. } A = \log x \cdot \log y$$

$$\text{II. } A = y^x$$

$$\text{VI. } A^y = Bx^C$$

$$\text{III. } A^y = B \cdot \frac{1}{x}$$

$$\text{VII. } \frac{A}{y} = B - C \cdot \frac{1}{\log x}$$

$$\text{IV. } \log y = A + B \cdot \frac{1}{x}$$

$$\text{VIII. } \frac{A}{y^2} = B \cdot \frac{1}{C - x^3}$$

3. Treat the data given below by the methods of mathematical statistics, assuming the confidence level to be equal to 0.95 (95%).

Use the following criteria to estimate errors: Q in Examples I-IV; $\varepsilon_\alpha \sqrt{2}$ in Examples V and VI; $3s/\sqrt{n}$ in Examples VII and VIII.

I. The per cent of iron in the ore: 55.56, 54.80, 55.30, 55.86, 53.56, 55.75, 55.50, 55.65, 56.00, 55.40.

TABLE 6

| Variant | Equation | A | B | C | D |
|---------|-------------------------------------|-------------|-------------|-------------|-------------|
| I | $x = \frac{A+B-2D}{C}$ | 58.02±0.01 | 21.6±0.2 | 0.854±0.001 | 0.850±0.005 |
| II | $x = \frac{A+5C}{BD}$ | 10.80±0.03 | 0.56±0.02 | 100.5±0.5 | 21.75±0.05 |
| III | $x = \frac{AC}{B+D}$ | 10.5±0.1 | 2.68±0.04 | 2.0±0.1 | 10.56±0.02 |
| IV | $x = \frac{(A^3-B^2)C}{D}$ | 5.68±0.01 | 1.542±0.002 | 21.6±0.02 | 4.00±0.01 |
| V | $x = \frac{A \log B}{5C-D}$ | 124.6±0.3 | 18.96±0.02 | 1.65±0.05 | 0.056±0.001 |
| VI | $x = \frac{\log A \log B^2}{CD}$ | 0.654±0.002 | 2.8±0.02 | 0.865±0.005 | 4.0±0.5 |
| VII | $x = \log A \log B_C^D$ | 2.6±0.2 | 57.5±0.5 | 265±2 | 1.2±0.2 |
| VIII | $x = \frac{A-10B}{\log C - \log D}$ | 25±1 | 0.65±0.05 | 280±5 | 5.67±0.01 |

II. The percentage content of phosphorus in steel: 0.056, 0.057, 0.051, 0.062, 0.054, 0.055, 0.058, 0.046, 0.053, 0.056.

III. The content of copper in semiconducting germanium (in per cent $\times 10^5$): 3.0, 4.0, 4.0, 5.0, 2.0, 4.0, 1.0, 8.0, 7.0, 3.0.

IV. The amount of barium sulphate (in mg) produced from a 1-g sample of a salt: 256.3, 260.1, 260.2, 258.6, 250.3, 240.5, 253.6, 251.8, 257.0, 260.1.

Calculate the percentage content of barium.

V. The volumes (in ml) of a 0.1N solution of $K_2Cr_2O_7$ used up for the titration of a solution of $FeSO_4$: 20.65, 21.00, 20.64, 20.54, 20.32, 20.60, 20.55, 20.60, 19.98, 20.65.

Calculate the content of iron (in mg).

VI. The quantities of lead dioxide (in mg) produced from a 0.5-g sample of bronze are as follows: 58.6, 51.0, 57.8, 54.3, 55.5, 55.7, 50.7, 41.8, 56.1, 59.5.

Calculate the percentage content of lead.

VII. The volumes (in ml) of a 0.15N solution of HCl used up for the titration of 25 ml of a NaOH solution are: 5.76, 5.60, 5.86, 5.68, 5.65, 5.61, 5.70, 5.43, 5.65, 5.68.

Find the normality of the NaOH solution.

VIII. The percentage content of chromium in steel: 2.64, 2.59, 2.65, 2.65, 2.60, 2.58, 2.65, 2.60, 2.64, 2.69.

3. PROBLEMS

SECTION A

1. In determining copper in a mineral sample weighing 1.5000 g the following amounts of copper oxide were found (in mg): 580, 585, 545, 578, 592, 588, 580, 584, 602, 587, 586, 581, 579, 587.

Determine the average content of copper in the mineral and $\epsilon_{0.95}$.

2. When analysing a standard sample of bronze containing 10.45 per cent of zinc two analysts obtained the following values for the amount of zinc:

| | | | | | |
|--------------|-------|-------|-------|-------|-------|
| I | 10.41 | 10.48 | 10.65 | 10.44 | 10.45 |
| II | 10.48 | 10.54 | 10.50 | 10.58 | 10.57 |
| I | 10.45 | 10.28 | 10.41 | 10.40 | 10.47 |
| II | 10.56 | 10.55 | 10.56 | 10.50 | 10.53 |

Determine the average content of zinc from the data obtained by each analyst, $\varepsilon_{0.95}$ and the systematic error, and estimate their work.

3. To determine copper in a solution three analysts obtained the results given in Table 7.

TABLE 7

| Copper taken, g | Copper found, g | | | Copper taken, g | Copper found, g | | |
|--------------------|-----------------|--------|--------|--------------------|-----------------|--------|--------|
| | 1 | 2 | 3 | | 1 | 2 | 3 |
| 0.0623 | 0.0613 | 0.0635 | 0.0622 | 0.2152 | 0.2142 | 0.2165 | 0.2150 |
| 0.0950 | 0.0938 | 0.0952 | 0.0955 | 0.2541 | 0.2533 | 0.2538 | 0.2545 |
| 0.1246 | 0.1238 | 0.1254 | 0.1240 | 0.2867 | 0.2870 | 0.2869 | 0.2867 |
| 0.1532 | 0.1521 | 0.1525 | 0.1535 | 0.3100 | 0.3100 | 0.3096 | 0.3098 |
| 0.1878 | 0.1869 | 0.1858 | 0.1882 | 0.3876 | 0.3875 | 0.3884 | 0.3880 |

Calculate the accuracy of the determination carried out by each analyst and figure out the possible systematic errors.

4. The following results were obtained in a colorimetric determination of zinc:

| | | | | | | | | |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Zinc taken, μg . . . | 20 | 30 | 40 | 50 | 60 | 80 | 100 | 120 |
| Zinc found, μg . . . | 19.2 | 28.7 | 37.4 | 45.2 | 54.2 | 75.8 | 96.8 | 119.4 |
| Zinc taken, μg . . . | 140 | 160 | 180 | 200 | 220 | 240 | 260 | 280 |
| Zinc found, μg . . . | 139.1 | 160.1 | 180.4 | 201.0 | 221.8 | 242.0 | 263.2 | 284.0 |

Find the standard deviation of a single determination and draw conclusions as to the presence of a systematic error in the determination of zinc by the given colorimetric method.

5. In calibrating a milliammeter with a silver coulometer the following amounts of deposited silver were obtained for 60 minutes at different currents:

| | | | | | |
|----------------------------------|------|-------|-------|-------|-------|
| Current, mA | 10 | 25 | 50 | 75 | 100 |
| Mass of silver deposit, mg . . . | 42.5 | 101.9 | 201.5 | 299.0 | 395.5 |

Construct a calibration graph for the milliammeter and determine the true current intensity if the milliammeter indicates 85 mA.

6. In calibrating a burette the following volumes of emerging water were obtained:

| Burette reading, ml | Volume of emerging water, ml | | | |
|---------------------|------------------------------|-------|-------|-------|
| 5 | 4.90 | 4.92 | 4.90 | 4.95 |
| 10 | 9.88 | 9.90 | 9.86 | 9.87 |
| 15 | 15.02 | 15.04 | 15.00 | 14.98 |
| 20 | 20.12 | 20.10 | 20.14 | 20.15 |
| 25 | 25.04 | 25.08 | 25.08 | 25.10 |

Plot a calibration graph and determine the true volume if the volume readings on the burette are 12.72 and 18.56 ml.

7. The molecular weight of a dissolved substance is determined from the depression of the freezing point of the solution by the formula

$$M = 1850 \frac{m}{V\Delta T}$$

where m = weighed portion of substance, $m = (1.4986 \pm \pm 0.0002)$ g

V = volume of water in which the weighed portion of substance is dissolved, $V = (25.34 \pm 0.05)$ ml

ΔT = lowering of the freezing point, $\Delta T = (1.25 \pm \pm 0.01)^\circ\text{C}$.

In this and succeeding problems the numbers 0.0002, 0.05 and 0.01 are the standard deviations for the values measured.

Find the accuracy and relative error of the determination and indicate which measurement gives the greatest error.

8. In a certain measurement the calculation is made with the aid of the formula

$$x = \frac{3.56^3 \sin 45^\circ 29' - \sqrt{0.687 \log 25.2 + 4.678}}{\sqrt{158.44} - \log 44.536 \log 5.92}$$

Calculate the value of x , rounding off the data according to the rules for treatment of observation results.

9. To determine the titre of a solution of KMnO_4 a weighed amount of oxalic acid, 1.0028 ± 0.0002 g, was dissolved in a measuring flask of 250.38 ± 0.05 ml capacity. From this

to a single elimination of errors by the criterion $\varepsilon_\alpha/\sqrt{2}$.

14. To determine the content of magnesium chloride in a brine, several 50-ml samples were diluted with water to 100 ml. The volumes (in ml) of a solution of complexon III with a titre of 0.00251 g/ml with respect to MgCl_2 used for the titration of 10 ml of these solutions in five series of experiments were as follows:

| | | | | | |
|---------------|-------|-------|-------|-------|-------|
| I | 20.52 | 20.48 | 20.60 | 20.45 | 20.52 |
| II | 20.53 | 20.53 | 20.47 | 20.58 | 20.51 |
| III | 20.35 | 20.38 | 20.28 | 20.33 | 20.31 |
| IV | 20.59 | 20.45 | 20.50 | 20.62 | 20.47 |
| V | 20.23 | 20.56 | 20.42 | 20.84 | 20.60 |

Determine the average content of magnesium chloride in the brine, calculate $\varepsilon_{0.95}$ and find out, through the use of the criterion Q , whether there are crude errors.

15. A standard thermometer calibrated for 25°C is provided with a certificate containing the following data (in $^\circ\text{C}$):

| | | | | | | |
|-----------------------|------|-------|-------|-------|-------|-------|
| Temperature | 0 | 5 | 10 | 15 | 20 | 25 |
| Correction | 0.00 | -0.01 | -0.04 | -0.06 | -0.02 | +0.04 |

In comparing the calibrated thermometer with the standard thermometer the following temperatures were noted (in $^\circ\text{C}$):

| | | | | | | |
|--------------------------|------|------|-------|-------|-------|-------|
| Calibrated thermometer | 0.00 | 6.00 | 11.00 | 14.00 | 21.00 | 25.00 |
| Standard thermometer . . | 0.02 | 6.04 | 11.08 | 14.10 | 20.98 | 24.94 |

Construct a correction graph for the calibrated thermometer and determine the true temperature if its readings are 7.85 and 18.22°C .

16. The specific heat capacity of a substance is determined from the formula

$$c = \frac{M(t_{\text{fn}} - t_{\text{ln}})}{m(t - t_{\text{fn}})}$$

where M = mass of water corrected for the mass of the calorimeter, $M = 500.4 \pm 0.2$ g

m = mass of the substance being examined, $m = 120.5$ g

t = temperature of the solid body before immersion into water, $t = (85.4 \pm 0.1)^\circ\text{C}$

t_{fin} = final temperature of water, $t_{\text{fin}} = (18.4 \pm 0.1)^\circ\text{C}$

t_{in} = initial temperature of water, $t_{\text{in}} = (20.3 \pm 0.1)^\circ\text{C}$.

Determine the specific heat capacity of the substance and the relative error of the determination and find out which of the measurements made gives the greatest error.

17. In a photometric determination of ammonia the following readings Δ were obtained on the scale of a photoelectric colorimeter versus the concentration of ammonia:

| | | | | | | |
|----------------------------------|------|------|------|------|------|------|
| Concentration, g/litre | 0.96 | 1.28 | 1.44 | 1.76 | 1.92 | 2.08 |
| Scale reading | 27.5 | 38.1 | 45.7 | 59.1 | 69.0 | 82.4 |

Plot a graph of scale readings against concentration on a logarithmic scale and calculate the coefficients in the equation

$$\log C = A + B \log \Delta$$

Determine the accuracy with which this relation is fulfilled, on the basis of the experimental data given above.

18. The molar refraction is determined by the formula

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$$

Find R and the relative error of the determination if the mass of 1 mole of a substance is $M = 78.12 \pm 0.02$ and the density $d = 0.8790 \pm 0.0005$; the refractive index $n = 1.5016 \pm 0.0002$.

Find out which of the measurements carried out yields the largest error.

19. The viscosity coefficient of a substance at different temperatures has the following values:

| | | | | | |
|---|------|------|------|------|------|
| Temperature, $^\circ\text{K}$ | 273 | 293 | 307 | 371 | 476 |
| Viscosity, cp | 1.66 | 1.55 | 1.48 | 1.26 | 1.08 |

Figure out the coefficients in the following equation representing viscosity versus temperature:

$$\log \eta = A + \frac{B}{T}$$

Determine the viscosity at a temperature of 350 °K and find out to what temperature there corresponds the viscosity 1.35 cp.

20. The distribution of salicylic acid between water and benzene is characterized by the following concentrations of the acid in the layers (in moles/litre $\cdot 10^{-3}$):

| | | | | | | |
|--------------------------------|------|------|------|--------|--------|--------|
| In the aqueous layer . . . | 3.63 | 6.68 | 9.40 | 12.60 | 21.00 | 28.30 |
| In the benzene layer . . . | 1.84 | 5.04 | 9.77 | 14.60 | 32.90 | 53.30 |
| In the aqueous layer | | | | 55.80 | 75.60 | 91.20 |
| In the benzene layer | | | | 165.00 | 281.00 | 434.00 |

Find the coefficients in the distribution equation if it has the form

$$\frac{C_w^n}{C_b} = K$$

where K and n are constants.

Find the concentration of salicylic acid at which it is distributed in the aqueous and benzene layers in a ratio of 1 to 2.5. What is the concentration of salicylic acid in the aqueous layer if its concentration in the benzene layer is 0.1 mole/litre?

21. The variables are interrelated by the following equations:

$$2 + \log y = A (\sin x)^b$$

$$10^y = A + \frac{B}{\sin x}$$

$$\log y = \frac{A}{B + \log(x/C)}$$

Find the systems of coordinates in which the relations between x and y could be expressed by a straight line.

SECTION C

22. Three analysts determined the various constituents of a crystal hydrate of copper sulphate, using duplicate 0.5000-g samples. The first analyst determined copper in terms of copper oxide and found the following amounts of

CuO: 0.1875, 0.1864, 0.1869, 0.1874, 0.1880 g. The second analyst determined sulphur as barium sulphate and the amounts of BaSO₄ he found were as follows: 0.5450, 0.5441, 0.5452, 0.5445, 0.5450 g. The third analyst determined water and obtained the following results: 0.0290, 0.0302, 0.0295, 0.0298, 0.0301 g.

Determine the composition of the crystal hydrate and estimate the work done by each analyst on the basis of the criterion $\varepsilon_{0.95}$.

23**. Nickel ore was analysed by different methods. In one of them, a sample of the ore was dissolved in acid and treated appropriately. The content of nickel was determined in duplicate samples from the colour intensity of the coloured solution. The following values were obtained (in per cent): 2.54, 2.60, 2.55, 2.58, 2.55, 2.59, 2.55, 2.57, 2.54.

In another experiment the solutions of weighed portions of the ore were divided into four aliquots in which the nickel was also determined colorimetrically. The aliquots (I, II, III, IV) were found to contain the following amounts of nickel (in per cent):

| | | | | | | |
|-----|-----------|------|------|------|------|------|
| I | | 2.41 | 2.43 | 2.39 | 2.40 | 2.41 |
| II | | 2.55 | 2.54 | 2.58 | 2.55 | 2.56 |
| III | | 2.45 | 2.48 | 2.47 | 2.50 | 2.46 |
| IV | | 2.65 | 2.58 | 2.63 | 2.67 | 2.61 |

In still another experiment four portions of the ore were weighed out for analysis and dissolved; three aliquots of each of the solutions were taken and the nickel was determined colorimetrically twice in each aliquot. The percentage content of nickel in each weighed portion was as follows:

| | | I | | II | | III | |
|----------|-----------|------|------|------|------|------|------|
| Sample 1 | | 2.45 | 2.41 | 2.51 | 2.54 | 2.38 | 2.39 |
| 2 | | 2.61 | 2.57 | 2.70 | 2.65 | 2.61 | 2.66 |
| 3 | | 2.34 | 2.36 | 2.41 | 2.39 | 2.36 | 2.38 |
| 4 | | 2.45 | 2.48 | 2.54 | 2.51 | 2.63 | 2.61 |

Determine the average content of nickel in the ore (in per cent) for the indicated series of experiments and the value of $\varepsilon_{0.95}$.

Test the significance of the data obtained in different series of experiments by using the criterion F . Draw a conclusion as to the most efficient procedure for sampling and treating samples.

24**. In determining manganese in steel with the use of different sampling techniques (shown schematically in

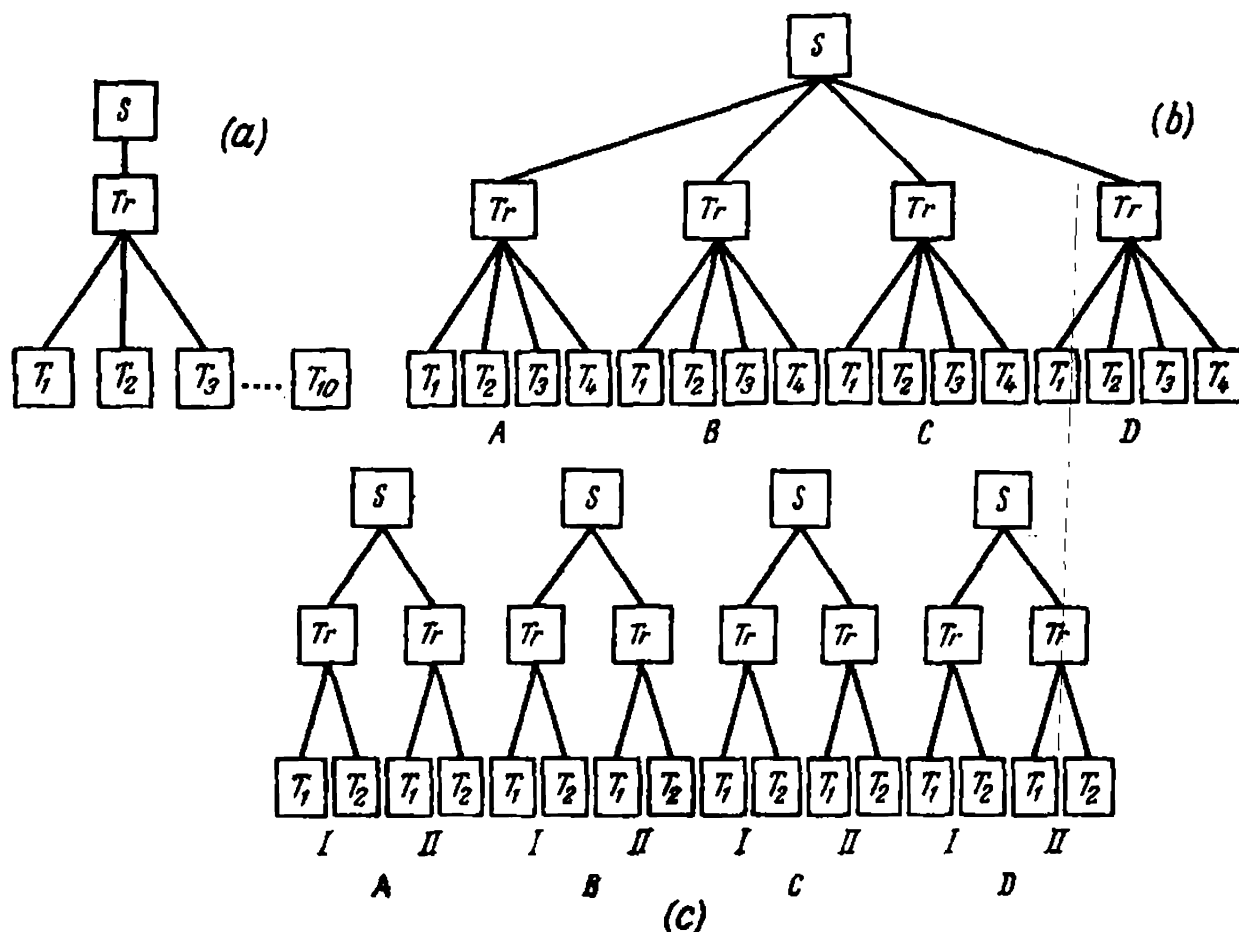


Figure 3. Sampling schemes: S—sample (weighed); Tr—treatment; T—titration.

Fig. 3) the following percentage contents of manganese were found in duplicate determinations:

- (a) when taking samples according to scheme a —1.25, 1.24, 1.26, 1.26, 1.25, 1.24, 1.23, 1.25, 1.26;
- (b) when taking samples according to scheme b

| | T_1 | T_2 | T_3 | T_4 |
|---------------|-------|-------|-------|-------|
| A | 1.22 | 1.25 | 1.25 | 2.23 |
| B | 1.28 | 1.30 | 1.27 | 1.31 |
| C | 1.18 | 1.20 | 1.17 | 1.20 |
| D | 1.24 | 1.25 | 1.24 | 1.26 |

(c) when taking samples according to scheme *c*

| | I | | II | |
|--------------------|------|------|------|------|
| <i>A</i> | 1.18 | 1.26 | 1.20 | 1.22 |
| <i>B</i> | 1.31 | 1.26 | 1.25 | 1.29 |
| <i>C</i> | 1.24 | 1.32 | 1.27 | 1.17 |
| <i>D</i> | 1.22 | 1.31 | 1.25 | 1.27 |

Determine the value of $\epsilon_{0.95}$ at each stage of the analysis and draw up the most efficient scheme for sampling.

25. When a sample of zinc ore containing 3.57 per cent of zinc was analysed by a new method, the following results were obtained in duplicate determinations: 3.57, 3.55, 3.68, 3.81, 3.56, 3.45, 3.55, 3.65, 3.54, 3.41, 3.40, 3.52, 3.76, 3.42, 3.47, 3.50, 3.55, 3.21, 3.45, 3.41, 3.52, 3.45, 3.65, 3.42, 3.57, 3.30, 3.43, 3.46, 3.57, 3.84, 3.43, 3.43, 3.58, 3.90, 3.44, 3.41, 3.48, 3.25, 3.45, 3.41, 3.41, 3.41, 3.57, 3.51, 3.42, 3.43, 3.59, 3.24, 3.41, 3.44.

Determine the average value of the analytical results obtained and find out whether there are random and systematic errors. Calculate $\epsilon_{0.95}$ for these data. Estimate these data by using the criterion *Q*.

26*. In calibrating a thermocouple use was made of the melting points of pure metals. The following millivoltmeter readings were taken (in mV):

| | | | | | |
|--------------------|------|------|------|------|------|
| Sodium | 0.98 | 0.98 | 1.02 | 1.00 | 1.01 |
| Indium | 1.30 | 1.37 | 1.36 | 1.34 | 1.38 |
| Bismuth | 2.10 | 2.15 | 2.12 | 2.13 | 2.10 |
| Lead | 2.45 | 2.43 | 2.56 | 2.42 | 2.47 |
| Antimony | 4.30 | 4.41 | 4.36 | 4.35 | 4.35 |
| Silver | 6.42 | 6.43 | 6.45 | 6.38 | 6.40 |

Plot a calibration graph for this thermocouple and deduce an equation relating the thermoelectromotive force to temperature. Estimate the precision to which the tabulated melting temperatures must be taken. To what temperature does the reading 1.85 mV correspond?

27*. For a 100-ml measuring flask the following values for the mass of water (in grams) were obtained in the flask at 28 °C with brass weights used for weighing: 99.576, 99.570, 99.580, 99.574, 99.572, 99.575, 99.573, 99.550, 99.570, 99.574.

Find the value of the correction for the temperature and the reduction for weighing with brass weights ("the mass in an empty space") and determine the true capacity of the flask.

28**. An investigation of the process of drying yielded the following data for the moisture content versus the time of drying:

| | | | | | | | |
|--------------------------|------|------|------|------|------|------|------|
| Time, min | 5 | 10 | 20 | 30 | 40 | 50 | 60 |
| Moisture, per cent . . . | 1.98 | 1.65 | 1.17 | 0.83 | 0.59 | 0.42 | 0.29 |

Find the initial moisture content in the material. Derive an equation relating the moisture content to the time of drying (of the type $C_0 - C_\tau = A + B \log \tau$, where C_0 is the initial moisture content). How long will it take to dry the material for the moisture content to decrease to 0.1 per cent?

29**. The solubility of chlorine in water at various temperatures and normal pressure has the following values:

| | | | | | | | |
|--|-------|-------|-------|-------|-------|-------|-------|
| Temperature, °K . . . | 273 | 283 | 293 | 303 | 313 | 323 | 333 |
| Solubility, g/100 g of water | 1.289 | 0.997 | 0.729 | 0.572 | 0.459 | 0.347 | 0.295 |

Derive the equation relating solubility to temperature. At what temperature will the solubility of chlorine at normal pressure be equal to 2 litres in 1 litre of water?

30. At different values of x the variable y assumes the following values:

| | | | | | | | | | | |
|-----------|------|------|------|------|------|------|-----|------|------|------|
| x . . . | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
| y . . . | 7.35 | 4.65 | 3.54 | 3.44 | 2.92 | 2.23 | 2.0 | 1.85 | 1.71 | 1.58 |

Find the equation relating y to x .

31. In the differential method of measurement the wavelength of light is calculated by the formula

$$\lambda = \frac{r^2(a+b)}{nab}$$

where λ = wavelength

r = aperture radius

a = distance from the aperture to the light source

b = distance from the aperture to the screen

n = constant integer.

Derive an equation for calculating the absolute and relative errors in measuring the wavelength $\Delta\lambda$ as a function of the measurement errors Δr , Δa , Δb .

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. How can the systematic error of an experiment be eliminated?

- (a) By carrying out repeated measurements.
- (b) By increasing the accuracy of measurements.
- (c) They cannot be eliminated.
- (d) They can be eliminated by calibration of the instruments used and by comparison with the reference standard.
- (e) To eliminate them it is sufficient to calibrate the instruments employed.

2. What experimental errors are called systematic?

- (a) Errors recurring from experiment to experiment.
- (b) Errors associated with measuring errors; such errors do not recur from experiment to experiment.
- (c) Errors resulting from the inaccuracy of the instruments used.
- (d) Errors due to the contamination of the reagents used.
- (e) Errors due to the method used, which repeat themselves from experiment to experiment.

3. The variables x and y are interrelated by the equation

$$\log y^2 = \frac{A}{Bx^3}$$

In which of the coordinate systems listed below will there exist a linear relationship between the functions x and y ?

- (a) $\log y$ vs. x^3 .
 - (b) y vs. x .
 - (c) $\log y$ vs. $\log x$.
 - (d) $\log y$ vs. $1/x^3$.
 - (e) $1/\log y$ vs. x .
 - (f) x^3 vs. $1/\log y$.
 - (g) y vs. $\log x$.
 - (h) $\log \log y$ vs. $\log x$.
4. What are the advantages of physicochemical methods of analysis?

(a) They enable one to determine the principal components of a substance with an accuracy of thousandths of a per cent.

(b) They can be widely used to automate analytical work.

(c) Some of the methods are highly selective and permit determination of 5 to 10 components at a time.

(d) They enable one to determine impurities with an accuracy of up to 10^{-5} per cent in very small portions of a substance, weighing tenths and hundredths of a milligram.

(e) These methods enable determination of impurities whose content ranges from 10^{-12} to 10^{-15} per cent.

(f) These methods can be used for analysis of very small volumes, up to 10^{-5} ml.

(g) They permit determination of all the elements of the Periodic Table at a time.

(h) They permit determination of impurities the content of which ranges from 10^{-6} to 10^{-9} per cent.

(i) They offer no special advantages.

5. The following volumes (in ml) of acid were used up to titrate 8 duplicate samples of a solution: 3.65, 3.72, 3.68, 3.31, 3.78, 3.72, 3.66, 3.70. The mean value calculated was 3.65 and the sum of the squares of deviations from the mean, 1.15. Find out which of the following suggestions is correct.

(a) The deviation of the mean is

$$\sqrt{\frac{1.15}{8}} = 0.38$$

(b) Since the difference is

$$3.65 - 3.31 \ll 3 \sqrt{\frac{1.15}{8}}$$

this measurement must not be rejected.

(c) The interval value of the volume at 0.95 confidence is

$$3.65 \pm 2.36 \sqrt{\frac{1.15}{7.8}}$$

(d) The interval value of the volume is

$$3.65 \pm \sqrt{\frac{1.15}{7.8}}$$

(e) The experiments carried out are inaccurate since the standard deviation of the mean is much greater than the accuracy of burette readings:

$$\sqrt{\frac{1.15}{7.8}} \gg 0.03$$

(f) Since the difference is

$$3.65 - 3.31 \gg 3 \sqrt{\frac{1.15}{7.8}}$$

this measurement should be rejected and the data recalculated.

(g) Since the difference is

$$3.65 - 3.31 \gg \sqrt{\frac{1.15}{7.8}} \times \sqrt{2}$$

this measurement should be rejected.

(h) The interval value of the volume at 0.95 confidence is

$$3.65 \pm \sqrt{\frac{1.15}{7}} \times 2.36$$

6. Which of the formulas under B is used to calculate the quantities listed under A?

| A | B |
|---|---|
| (a) The accuracy of a single measurement. | (1) $\sigma_{\bar{x}} = \frac{\bar{s}}{\sqrt{n}}$. |
| (b) Dispersion. | (2) $\bar{x} \pm \epsilon_{\alpha}$. |
| (c) Standard deviation. | (3) $R = x_{\max} - x_{\min}$. |
| (d) Confidence interval. | (4) $V = \frac{\sum d^2}{n-1}$. |
| (e) Standard deviation of the mean. | (5) $\epsilon_{\alpha} = \frac{st_{\alpha, h}}{\sqrt{n}}$. |
| (f) Range. | (6) $\bar{s} = \sqrt{\frac{\sum d^2}{n-1}}$. |

7. For the equations given under A find the coordinate system under B in which a linear relationship exists between the functions x and y .

| A | B |
|----------------------------------|----------------------------------|
| (a) $y = B - \frac{A}{x}$. | (1) y^2 vs. x^3 . |
| (b) $y = A \times 10^{\log x}$. | (2) x vs. y . |
| (c) $Ay^2 = Bx^3$. | (3) y^2 vs. $1/x^3$. |
| (d) $A/y = B + D/x$. | (4) y vs. $1/x$. |
| (e) $y^2x^3 = A$. | (5) $\log \log y$ vs. x . |
| (f) $\log y = B^x$. | (6) $\log \log y$ vs. $\log x$. |
| (g) $A^x = B^y$. | (7) $\log y$ vs. $\log x$. |
| (h) $\log y = A^{\log x}$. | (8) $1/y$ vs. $1/x$. |

8. Find the absolute error Δz under B and the relative error $\Delta z/z$ under C for the equations listed under A.

| A | B |
|-------------------------------|--|
| (a) $z = Axy$. | (1) $\Delta z = 2x\Delta x + 3y^2\Delta y$. |
| (b) $z = 1/x - 1/y$. | (2) $\Delta z = 4\Delta x + 10 \frac{\Delta y}{y^2}$. |
| (c) $z = x^2 - y^3$. | (3) $\Delta z = A \frac{x\Delta y + y\Delta x}{x^2y^2}$. |
| (d) $z = 4x - \frac{10}{y}$. | (4) $\Delta z = \frac{\Delta x}{x^2} + \frac{\Delta y}{y^2}$. |
| (e) $z = \frac{A}{xy}$. | (5) $\Delta z = 2xy^3\Delta x + 3x^2y^2\Delta y$. |
| (f) $z = 4x - 10y$. | (6) $\Delta z = Ax\Delta y + Ay\Delta x$. |
| (g) $z = x^2y^3$. | (7) $\Delta z = 4\Delta x + 10\Delta y$. |

| C |
|--|
| (1) $\frac{\Delta z}{z} = \frac{4x \frac{\Delta x}{x} + 10y \frac{\Delta y}{y}}{4x + 10y}$. |
| (2) $\frac{\Delta z}{z} = \frac{\Delta x}{x} + \frac{\Delta y}{y}$. |
| (3) $\frac{\Delta z}{z} = \frac{\Delta x}{x} - \frac{\Delta y}{y}$. |

$$(4) \quad \frac{\Delta z}{z} = \frac{\Delta x}{x} \cdot \frac{\Delta y}{y} .$$

$$(5) \quad \frac{\Delta z}{z} = \frac{2x \frac{\Delta x}{x} + 3y \frac{\Delta y}{y}}{x^2 + y^3} ,$$

$$(6) \quad \frac{\Delta z}{z} = \frac{x \frac{\Delta x}{x} + y \frac{\Delta y}{y}}{x^2 + y^3} .$$

$$(7) \quad \frac{\Delta z}{z} = 2 \frac{\Delta x}{x} + 3 \frac{\Delta y}{y} .$$

9. Indicate in Fig. 4 the graphs corresponding to the equations under A. Find, under B, the equation of the graph selected.

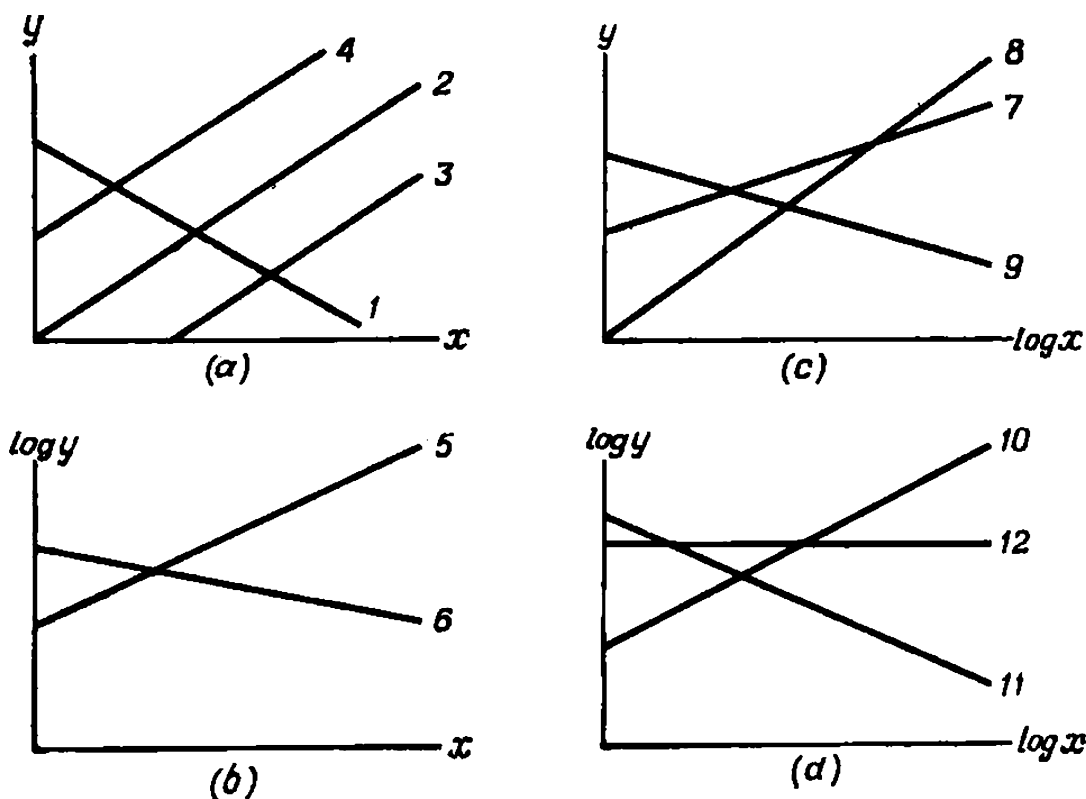


Figure 4

A

$$(a) \quad y^A = \frac{B}{x^D} .$$

$$(b) \quad y = Ax .$$

$$(c) \quad A^x = B^y .$$

$$(d) \quad y = \frac{10}{2x} .$$

B

$$(1) \quad f(x) \cdot f(y) = A .$$

$$(2) \quad \frac{f(x)}{f(y)} = A .$$

$$(3) \quad f(y) = Af(x) .$$

$$(4) \quad f(y) = A + \frac{B}{f(x)} .$$

$$(e) y = -10 + 4x. \quad (5) f(y) = A + Bf(x).$$

$$(f) y = 5x^2. \quad (6) f(y) = \frac{A}{f(x)}.$$

$$(g) x^2y^3 = A. \quad (7) f(y) = A - Bf(x).$$

$$(h) x^2 = 10^y. \quad (8) f(y) = A^{f(x)}.$$

10. When lead was determined six times in duplicate samples, the mean value was found to be equal to 1.25 per cent and the sum of the squares of the deviations from the mean, to 0.42. Indicate under A the formula which should be used to calculate the interval value of the lead content in the sample at the 0.95 confidence level ($t_{\alpha, 4} = 2.78$, $t_{\alpha, 5} = 2.57$, $t_{\alpha, 6} = 2.45$). Then find out the reason why the remaining formulas cannot be used for the purpose (see under B).

A

$$(a) x = 0.42 \pm \sqrt{\frac{1.25}{5.6}} \times 2.57 = 0.42 \pm 0.53.$$

$$(b) x = 1.25 \pm \sqrt{\frac{0.42}{6}} = 1.25 \pm 0.27.$$

$$(c) x = 1.25 \pm \frac{2.6 \sqrt{\frac{0.42}{5}}}{\sqrt{6}} = 1.2 \pm 0.3.$$

$$(d) x = 1.25 \pm \frac{2.57 \sqrt{\frac{0.42}{5}}}{\sqrt{6}} = 1.25 \pm 0.304.$$

$$(e) x = 1.25 \pm \frac{2.45 \sqrt{\frac{0.42}{5}}}{\sqrt{6}} = 1.2 \pm 0.3.$$

B

- (1) A wrong formula has been taken for calculations.
- (2) A wrong table value has been used for calculations.
- (3) The calculation has been made with superfluous accuracy.
- (4) The data have been incorrectly inserted into the correctly selected formula.
- (5) The accuracy of the calculation made is insufficient.

Colorimetry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. To work by the method of standard series a standard solution was prepared by dissolving 0.854 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1.00 litre of water. From this solution, to which ammonia was added, there were prepared 10 coloured standards containing from 1.00 to 10.00 ml of solution in 20.00 ml of water.

A sample of the substance being examined, weighing 0.520 gram, was dissolved in 250.0 ml of water. After 5.00 ml of the unknown solution reacted with an ammonia solution and was diluted to 20 ml the colour intensity of the solution was found to be equal to that of the eighth standard. Calculate the per cent of copper in the substance under study.

Solution: As stated in the problem, the colour intensity of copper in the unknown solution coincides with that of the eighth standard. The content of copper in the eighth standard (in grams) is equal to

$$G = \frac{0.854 \times 63.5 \times 8}{250 \times 1000} = 1.74 \times 10^{-3}$$

where 63.5 is the atomic weight of copper and 250 is the molecular weight of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Since the measuring error is 2-5 per cent, all calculations can be made accurate to the third significant digit.

According to the statement of the problem 1.74×10^{-3} g of copper corresponds to 5 ml of the unknown solution and hence the amount of copper (in grams) in the whole of the solution is

$$Q = \frac{1.74 \times 10^{-3} \times 250}{5} = 8.70 \times 10^{-2}$$

The percentage content of copper is equal to

$$C = \frac{8.70 \times 10^{-2}}{5.20 \times 10^{-1}} \times 100 = 16.8$$

Example 2. To determine chromium in steel a standard solution was prepared, containing 0.750 g of K_2CrO_4 in 250.0 ml of water.

A sample of the metal weighing 0.500 g was dissolved in acid and after the chromium was oxidized to chromate the solution was diluted with water to 200.0 ml. The resulting solution was compared with a standard, 6.80 ml of which was diluted with water to 25.00 ml in order to equalize the colour intensities. Calculate the percentage content of chromium in the steel.

Solution: The content of chromium in the reference solution is (in grams):

$$g = \frac{0.75 \times 52.0 \times 6.80}{194 \times 250} = 5.46 \times 10^{-3}$$

Since the colour intensities of the two solutions are the same and the volume and the chromium content of the reference solution are known, one can calculate the percentage of chromium in the unknown solution:

$$C = \frac{5.46 \times 10^{-3} \times 200 \times 100}{25.0 \times 0.5} = 8.75$$

Example 3. To determine manganese a standard 0.0100N solution of $KMnO_4$ was made (the normality was determined by the reaction with $H_2C_2O_4$).

From a 0.500-g sample of an alloy, after appropriate treatment, there was obtained 150.0 ml of a solution containing manganese in the form of $HMnO_4$. Three samples of the solution were matched with the standard in a colorimeter at $H_{st} = 5.00$ cm; the colour intensities were found to be equal at $H_x = 8.52, 8.50$, and 8.46 cm. Compute the percentage content of manganese in the alloy.

Solution: The arithmetic mean for H_x is

$$H_x = \frac{8.52 + 8.50 + 8.46}{3} = 8.49 \text{ cm}$$

Hence

$$C_x = \frac{0.01 \times 5}{8.49} = 0.0059N$$

Thus, the percentage content of manganese is equal to

$$C = \frac{0.0059 \times 11.0 \times 150 \times 100}{1000 \times 0.5} = 1.9$$

where 11.0 is the equivalent weight of Mn in KMnO_4 according to the reaction with $\text{H}_2\text{C}_2\text{O}_4$.

2. MULTIVARIANT PROBLEMS

1. Scales of standards were prepared for determinations to be carried out by the standard series method. By using the data given in Table 8, determine the concentrations of the solutions in terms of the units indicated in the table.

2. A standard solution was prepared for a colorimetric analysis to be carried out by the duplication method. The results obtained are tabulated in Table 9. Determine the concentrations of the solutions in terms of the units indicated in the table.

3. The data collected in Table 10 were obtained in colorimetric determinations made by the colour equalization method. Determine the concentrations of the solutions in terms of the units indicated.

3. PROBLEMS

SECTION A

1. When light is passed through a layer of solution of unit thickness (1 cm), its intensity decreases by 10 per cent.

What will be the intensity of light when it is passed through a layer of the same solution having a thickness of 10 cm?

2. To prepare a series of standards 25.00 ml of a 0.0150N solution of $\text{K}_2\text{Cr}_2\text{O}_7$ was diluted with water to 500.0 ml and 0.50, . . . , 10.00 ml of this solution were taken at an interval of 0.50 ml. To these were added the acid and diphenylcarbazide; the coloured solutions were diluted with water to 25.00 ml.

TABLE 8

| Variant | Standard solution | Reaction by which coloured substance is formed | Scale of standards | | | | | Volume of standard solution, ml | Standard of identical colour intensity | Substance to be determined and its concentration |
|---------|--|--|--|-------|-------|-------|-------|---------------------------------|--|--|
| | | | volumes of standard solutions taken for analysis, ml | | | | | | | |
| | | | 1 | 2 | 3 | 4 | 5 | | | |
| I | 0.0100 <i>N</i> solution of KMnO_4 | Intrinsic colour | 0.25 | 0.50 | 0.75 | 1.00 | 1.25 | 10 | 2 | KMnO_4 (in mg/ml) |
| II | 0.500 g CuSO_4 in 250 ml of solution | With ammonia | 2.00 | 4.00 | 6.00 | 8.00 | 10.00 | 50 | 4 | Cu (in mg/ml) |
| III | Solution with a titre of 1 mg/ml $\text{K}_2\text{Cr}_2\text{O}_7$ | Intrinsic colour | 10.0 | 15.0 | 20.0 | 25.0 | 30.0 | 100 | Between 2 and 3 | Molarity of solution |
| IV | 0.500 g FeCl_3 in 100 ml of solution | With KSCN | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 | 25 | Between 1 and 2 | Fe_2O_3 (in mg/ml) |
| V | 0.0250 <i>N</i> solution of K_2CrO_4 | With diphenylcarbazide | 5.00 | 5.50 | 6.00 | 6.50 | 7.00 | 25 | 4 | Cr (in per cent) in 1-g sample |
| VI | 0.0550 <i>N</i> solution of NH_4OH | With Nessler's reagent | 4.50 | 5.00 | 5.50 | 6.00 | 6.50 | 25 | 2 | NH_3 (in mg/ml) if 10 litres of gas are passed |
| VII | 1.50 g Na_2SO_3 in 50 ml of solution | With formaldehyde and fuchsin | 5.00 | 10.00 | 15.00 | 20.00 | 25.00 | 100 | 5 | SO_2 (in mg/l) after passage of 5 litres of gas |
| VIII | 0.500 g $(\text{NH}_4)_2\text{MoO}_4$ in 250 ml of solution | With dithiol | 3.00 | 6.00 | 9.00 | 12.00 | 15.00 | 25 | 1 | MoO_3 (in per cent) in mineral, the sample weighing 2 grams |

TABLE 9

| Variant | Standard solution | Reaction by which coloured substance is formed | Volume of solution, ml | | | Substance being determined and its concentration |
|---------|---|---|------------------------|---------|-----------------------------|--|
| | | | standard | unknown | after colours are equalized | |
| I | 0.050 g NiSO ₄ in 25 ml of solution | With dimethylglyoxime | 8.56 | 10 | 25 | Ni (in %) in steel; a 1.5-g sample |
| II | 0.05N KMnO ₄ solution | Intrinsic colour | 0.56 | 5 | 10 | Mn (in mg/100 ml) |
| III | 0.025N CuSO ₄ solution | With ammonia | 4.25 | 2.5 | 10 | CuSO ₄ (in mg/50 ml) |
| IV | 0.500 g NaNO ₂ in 25 ml of solution | With naphthylamino-sulphonic acid | 2.56 | 25 | 50 | NO ₂ (in mg/l) |
| V | 1 g Fe in 100 ml of solution | With sulphanilic acid | 15.2 | 50.0 | 100 | Fe ₂ O ₃ (in %) in mineral; a 2-g sample |
| VI | 0.250 g Cr ₂ (SO ₄) ₃ in 250 ml of solution | Formation of chromate after oxidation of chromium | 20.2 | 15.0 | 50 | Cr (in %) in steel; a 1-g sample |
| VII | 0.200 g TiO ₂ in 100 ml of solution | Formation of pertitanic acid | 6.85 | 25.0 | 25 | Ti (in mg/ml) |
| VIII | 0.25 g As ₂ O ₃ in 250 ml of solution | Formation of molybdenum blue | 22.35 | 50 | 50 | As (in mg/250 ml) |

TABLE 10

| Variant | Standard solution | Reaction by which coloured substance is formed | Thickness of solution layer, mm | | Substance being determined and its concentration |
|---------|--|---|---------------------------------|---------|---|
| | | | standard | unknown | |
| I | 0.500 g Na_2HPO_4 in 100 ml of solution | Formation of molybdenum blue | 85.6 | 48.9 | P_2O_5 (in mg/ml) |
| II | Solution of 0.1 g of standard sample containing 0.86 % Cr in 25 ml of solution | Formation of chromate after oxidation of chromium | 78.4 | 18.4 | Cr in steel when 0.25 g was dissolved in 25 ml of solution (in %) |
| III | 0.25 g Pb_3O_4 in 25 ml of solution | With dithizone | 36.2 | 82.0 | Pb (in mg/100 ml) |
| IV | 0.750 g AlCl_3 in 250 ml of solution | With aluminon | 48.3 | 53.4 | Al_2O_3 in mineral when 2 grams were dissolved in 100 ml of solution (in %) |
| V | 0.0685 g I_2 in 500 ml of solution | With starch | 12.8 | 96.4 | I_2 (in mg/litre) |
| VI | 0.0250 g Bi in 100 ml of solution | With diethyldithiocarbamate | 32.8 | 73.8 | Bi (in mg/250 ml) |
| VII | 0.256 g CoSO_4 in 0.5 l of solution | With nitroso-P-salt | 23.4 | 93.2 | Molarity of solution |
| VIII | 0.056 g Pb in 100 ml of solution | With phenylfluorone | 18.4 | 63.8 | Pb in metal when 0.1 g was dissolved in 250 ml of solution (in %) |

A sample of steel weighing 0.100 g was dissolved and the resulting solution diluted with water to 25.00 ml; five millilitres of the solution were taken and diluted, after appropriate treatment, to 25.00 ml with water. The colour intensity of this solution was found to lie between the colour intensities of the 11th and 12th standards.

Find the percentage content of chromium in the steel.

3. To prepare a series of standards, samples weighing 0.50, . . . , 5.00 ml were taken at an interval of 0.50 ml from a solution containing 0.648 g of NaNO_2 in 500.0 ml of water; to these portions there were added α -naphthylamine and sulphanilic acid and the coloured solutions were diluted with water to 20.00 ml.

A weighed amount of the salt (0.520 g) was dissolved in 250.0 ml of water and 5.00 ml of the solution was taken, which, after appropriate treatment, was diluted with water to 20.00 ml. The colour intensity of this solution was found to be equal to that of the 8th standard.

Determine the percentage content of NO_2^- in the salt.

4. To prepare a series of standards, 15.00 ml of a 0.0215N solution of KMnO_4 was diluted to 500.0 ml and 1.00, . . . , 10.00 ml of the solution were taken at an interval of 1 ml and diluted with water to 25.00 ml.

A sample of steel weighing 0.500 g was dissolved in acid, oxidized by ammonium persulphate and diluted with water to 100.0 ml. The colour intensity of this solution was found to be intermediate between the colour intensities of the 4th and 5th standards.

Find the per cent of manganese in the steel.

5. A sample of an iron(III) salt weighing 0.455 g was dissolved in 100.0 ml of water. From this solution there was taken 5.00 ml, which, after treatment with an ammonia solution and sulphosalicylic acid, gave 50.00 ml of a coloured solution. To obtain a solution of the same colour as the unknown solution, to 20 ml of a mixture of ammonia and sulphosalicylic acid there were added 12.80 ml of a solution, which contained 2.250 g of $\text{KFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 1.00 litre of water, and water to make up the volume to 50 ml.

Find the percentage of iron in the salt.

6. An amount of natural water containing chlorides was diluted tenfold with distilled water. To 15.00 ml of this

water there were added 10.00 ml of a dye and 5.00 ml of distilled water. To obtain a solution of the same colour as the unknown solution, to 10 ml of the dye there was added 2.50 ml of a 0.00500M sodium chloride solution and distilled water to make up the volume to 30 ml.

Determine the concentration of chloride in natural water (in mg/litre).

7. To determine the content of iron in natural water, 25.00 ml of this water was treated with hydrogen peroxide and ammonium persulphate and after the addition of KSCN the volume of the sample was made up to 50.00 ml with distilled water. A standard solution was prepared by dissolving 0.863 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in 100 ml of water. To prepare a solution of the same colour as the unknown solution, to 20 ml of an aqueous solution of potassium rhodanide there was added 5.50 ml of the standard solution and the volume was made up to 50.00 ml with distilled water.

Determine the iron content (in mg/litre) in the water being analysed.

8. A sample of steel weighing 0.325 g was dissolved in acid and after chromium was oxidized by ammonium persulphate 25.00 ml of a coloured solution was obtained; 10.00 ml of this solution was diluted with water to 50.00 ml. A standard solution was made by dissolving 0.125 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 250.0 ml of water. To prepare a solution of the same colour as the unknown solution, 12.5 ml of the standard solution was diluted with distilled water to 50 ml.

Determine the percentage content of chromium in the steel.

9. A sample of a metal weighing 0.500 g was dissolved and the manganese present was oxidized to MnO_4^- . The volume of the solution at this point was made up to 100.0 ml. A 0.0100N solution of KMnO_4 was used as a standard. When compared in a colorimeter the colour intensities of the standard and unknown solutions were found to be equal at layer thicknesses of 5 and 8.49 cm, respectively.

Determine the per cent of manganese in the metal.

10. To determine zinc impurity in an impure copper salt, a portion of the salt weighing 1.500 g was dissolved in 25 ml of water. After appropriate treatment 5.00 ml of this solu-

tion gave 50.00 ml of a coloured solution. A standard solution was prepared by dissolving 100 mg of zinc chloride in 100.0 ml of water. When treated appropriately 2.50 ml of the standard solution gave 25.00 ml of a coloured solution. The colour intensities of the standard and unknown solutions were found to be the same at layer thicknesses of 3.00 and 8.25 cm, respectively.

Determine the percentage content of zinc in the copper salt.

11. A 1.500-g sample of a titanium-containing mineral was dissolved and treated with hydrogen peroxide. This gave 250.0 ml of a coloured solution. A solution containing 0.200 g of titanium in one litre was used as a standard. The colour intensities of the standard and unknown solutions were found to be equal at layer thicknesses of 10 and 6.70 cm, respectively.

Determine the percentage content of TiO_2 in the mineral.

12. A sample of natural water containing NO_3^- was treated with silver sulphate to remove the chloride ion present and then with phenoldisulphonic acid. A 0.00500N solution of sodium nitrate coloured with phenoldisulphonic acid was used as a standard. Three water samples were matched with the standard solution. Their colour intensities were found to be the same at $H_{st} = 5$ cm and at the following values of H_x : 6.50, 6.60, and 6.45 cm.

Determine the concentration, in mg/litre, of NO_3^- in the water.

SECTION B

13. What is the layer thickness of a coloured solution needed to decrease the radiant power of the incident beam of light by a factor of 10 if the molar absorptivity (molar extinction coefficient) is 4750 and the concentration, 1×10^{-3} mole/litre?

14. To prepare a series of standards a sample of pure nickel weighing 0.158 g was dissolved in nitric acid and the resulting solution diluted with water to 250 ml. From this solution 0.25, . . . , 5 ml were taken at an interval of 0.25 ml, the volumes of the solutions were made up to 10 ml and the nickel was oxidized by bromine to the trivalent state.

Nickel(III) combined with dimethylglyoxime forms a coloured complex.

A 0.250-g sample of steel containing nickel was dissolved in acid. The volume of the resulting solution was made up to 100 ml by adding water to it and 2.00 ml of this solution was treated appropriately and then diluted with water to 10.0 ml. The colour intensity of the solution obtained was found to be intermediate between the colour intensities of the 14th and 15th standards, being closer to the latter.

Determine the percentage content of nickel in the steel.

15. To determine sulphurous anhydride in a gas a scale of imitative solutions, each of 15 ml in volume, was prepared, their colours corresponding to the following amounts of SO_2 :

| | | | | | | | | | | |
|---|---|------|------|------|------|-----|-----|-----|-----|-----|
| No. of test tube . . . | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Content of SO_2 , $\mu\text{g/ml}$ | 0 | 10.0 | 30.0 | 50.0 | 75.0 | 100 | 125 | 150 | 200 | 250 |

A 500- cm^3 volume of the gas was bubbled through the absorbing solution at 22 °C and 750 mm Hg and diluted to 100.0 ml in a measuring flask; 10 ml of the solution with a fuchsinformaldehyde reagent gave 15.00 ml of a coloured solution, its colour intensity being intermediate between the 4th and 5th standards.

Determine the concentration, in moles per litre, of SO_2 in the gas.

16*. To prepare a standard solution a 0.801-g sample of a crystal hydrate of nickel chloride containing 15.5 per cent of water was dissolved in 100.0 ml of water. From this solution 2.00, . . . , 20.00 ml were measured, at intervals of 2.00 ml, into 50.00-ml measuring flasks, and coloured compounds of nickel with diethyldithiocarbamate in ammonia solution were obtained..

A 25.00-ml sample of the solution was taken from a nickel-plating bath and diluted to 50.0 ml. After appropriate treatment 5.00 ml of this solution was diluted to 100.0 ml. The colour intensity of the solution was found to be intermediate between the 7th and 6th standards.

How much of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (in kg) must be taken to prepare 500 litres of a nickel-plating solution of the indicated composition?

17. A 0.256-g sample of an iron-containing mineral was dissolved and diluted with water to 100.0 ml; 5.00 ml of this solution was treated with 10.00 ml of ammonium rhodanide. A standard solution was prepared by dissolving 0.135 g of an iron salt, containing 10.5 per cent of iron, in 250.0 ml of water. In an analysis by the duplication method, for the colours to be equalized, 8.50 ml of the standard solution was added to 10.00 ml of the ammonium rhodanide solution and 3.50 ml of water to the unknown solution.

Determine the percentage of iron oxide in the mineral.

18. To determine iodide in natural water 500 ml of the water was evaporated to 10 ml, and the iodide oxidized to iodine by potassium dichromate; after starch was added 25.00 ml of a coloured solution was obtained, which was transferred into the left-hand cuvette of a colorimeter. A reference solution was prepared by dissolving 0.150 g of potassium iodide, containing 6.8 per cent of water and 0.5 per cent of sodium chloride, in 1 litre of water. After being treated as indicated above 1.00 ml of this solution gave 50.00 ml of a coloured solution, which was transferred into the right-hand cuvette. The colour intensities were found to be the same with the layer thickness of the standard solution being 5.00 cm and those of the unknown solutions, 6.85, 6.83, and 6.86 cm. The corrections for the cuvettes are: $\Delta L_r = -0.04$ cm and $\Delta L_l = +0.02$ cm.

Determine the iodine content of the water being analysed (in mg/litre). What error would be introduced into the result obtained if the impurities in the potassium iodide and the corrections for the colorimeter cuvettes were not taken into account?

19. A sample of molybdenum oxide weighing 0.050 ± 0.002 g and containing 0.025 per cent of contaminants was dissolved and treated with dithiol. The coloured solution obtained (50.00 ± 0.05 ml) after extraction was transferred into the right-hand cuvette of a colorimeter. A sample of a mineral weighing 2.250 ± 0.005 g was dissolved and after the same treatment as above 100.000 ± 0.005 ml of a coloured solution was obtained, which was placed in the left-hand cuvette. The colour intensities of the solutions were found to be equal with the layer thickness of the stan-

dard solution being 5.00 ± 0.02 cm and that of the unknown, 9.16 ± 0.02 cm.

Determine the percentage content of molybdenum oxide in the mineral and the measuring error. Which of the operations performed introduces the greatest error into the measurement?

20**. A 1.535-g sample of semiconducting germanium containing manganese was dissolved and the solution diluted with water to 10.00 ml. From this solution a 2.00-ml portion was oxidized by ammonium persulphate, which resulted in 10.00 ml of a coloured solution. The standard solution used was a solution of KMnO_4 having a titre of 0.000156 mg/ml with respect to oxalic acid, 5 ml of the solution being diluted to 500.00 ml. The standard and unknown solutions showed the same colour intensity at layer thicknesses of 7.75 and 4.75 cm, respectively.

Determine the concentration of manganese (in atoms/cm³).

21. In a colorimeter, the thickness of an absorbing layer may change from 2 to 98 mm.

Within what limits can one determine the unknown concentration if the concentration of the reference solution is 10 mg/ml?

22**. The sensitivity of a colorimetric determination of nickel with the aid of dimethylglyoxime under certain conditions is 3 μg in 50.00 ml of solution.

Can one determine the content of nickel in semiconducting selenium by this method given that its concentration is 10^{19} atoms/cm³? What is the weight of the sample that must be dissolved in 10 ml of solvent? (The density of monoclinic crystalline selenium is 4.46 g/cm³.)

23. To determine gold by its reaction with *o*-tolidine a standard solution was prepared, containing 0.0027 $\mu\text{g}/\text{ml}$ of gold.

This solution was used to prepare a series of standards—10 standards totalling 15.00 ml at an interval of 1.00 ml.

A 0.567-g sample of a metal was dissolved in acid and the resulting solution was diluted with water to 50.00 ml; after appropriate treatment 2.50 ml of this solution was diluted with water to 10.00 ml. The colour intensity of the solution was found to be equal to that of the 7th standard.

Determine the percentage of gold in the metal.

24. A standard solution was prepared by dissolving 0.125 g of lead nitrate in 1.00 litre of water; 5.00 ml of this solution was treated with diphenylthiocarbazone (dithizone) and diluted to 50.00 ml. The coloured complex was extracted with 10.00 ml of chloroform.

A 1.350-g sample of a semiconducting alloy was dissolved and the resulting solution diluted with water to 50.00 ml; 1.00 ml of this solution was diluted with water to 25.00 ml. The coloured complex was extracted with 5.00 ml of chloroform. The colour intensities of the standard and the extract were found to be the same with the layer thicknesses of the standard and unknown solutions being 5 and 8.15 cm, respectively.

Determine the percentage content of lead in the alloy.

25. To determine As_2O_3 in air a standard solution was made by dissolving 0.256 g of a crystal hydrate of disubstituted sodium arsenite in 500.0 ml of water. To 1.00 ml of this solution there was added a solution of molybdenum and hydrazine sulphate and the resulting solution was diluted with water to 25.00 ml.

A 100-litre volume of air containing As_2O_3 was passed through the absorbing solution and after appropriate treatment 50 ml of a coloured solution was obtained. The colour intensities of the standard and unknown solutions were found to be equal at layer thicknesses of 5.00 and 6.25 cm, respectively.

Determine the concentration of As_2O_3 in the air (in mg/m^3) and find its excess over the permissible limit ($0.3 \text{ mg}/\text{m}^3$).

26. To prepare a reference solution 1.00 ml of a standard solution of KMnO_4 having a titre of 0.0000234 g/ml with respect to iron was diluted with water to 50.00 ml. A 0.533-g sample of silicon was dissolved and the resulting solution diluted with water to 10.00 ml. The treatment of 1.00 ml of this solution with periodate in the presence of phosphoric acid resulted in 25.00 ml of a coloured solution. The colour intensities of the standard and unknown solutions were found to be the same at layer thicknesses of 7.50 and 5.35 cm, respectively.

Determine the percentage content of Mn in the silicon. Is it possible, by using this standard solution, to determine the permissible content of manganese in semiconducting

silicon if it is of the order of 10^{-3} per cent? Under what conditions must this determination be carried out?

27. To determine chromium in steel, two standard samples of steel were used, one containing 1.40 and the other 0.05 per cent of chromium. When a sample of steel of unknown composition was dissolved and oxidized by periodate, 25.00 ml of a coloured solution was obtained. When the standard samples of the same weight were dissolved and treated in an analogous way, it was found that the colour intensities of the first standard solution and the unknown sample were the same at layer thicknesses of 2 and 10 cm, respectively, and those of the second standard solution and the unknown sample were found to be equal at layer thicknesses of 10 and 2 cm, respectively.

For comparison, 25 ml of a solution was prepared from a mixture of 0.200 g of the first and 0.300 g of the second standard. The colour intensities of the standard and unknown solutions were found to be the same at layer thicknesses of 5.00 and 4.00 cm, respectively.

Determine the percentage of chromium in the steel.

28. For a determination of phosphorus a 0.5265 ± 0.0002 -g sample of a standard containing 6.5 ± 0.1 per cent of phosphorus was dissolved in a measuring flask of 10.15 ± 0.01 -ml capacity and the resulting solution was diluted to the mark. This solution was then pipetted into a 50-ml measuring flask with a pipette of 2.02 ± 0.01 -ml capacity. The solution was treated with molybdate and vanadate solutions and, as a result, 50.12 ± 0.02 ml of a coloured solution was obtained.

A sample of steel weighing 0.3560 ± 0.0002 g was dissolved and treated as indicated above; as a result, 25.05 ± 0.02 ml of a coloured solution was obtained. The colour intensities of the standard and unknown solutions were found to be equal at layer thicknesses of 5.00 ± 0.05 and 7.25 ± 0.05 cm, respectively.

Determine the percentage of phosphorus in the sample and the measuring error. Find out which measurements give the greatest error. With what precision must all the measurements be carried out for the errors to be of the same order?

29. A standard solution was prepared by passing 2.00 litres of air saturated at 20°C with vapours of methanol

through 100.0 ml of an absorbing solution. To determine the concentration of methanol in the air of production premises 25.00 litres of the air was passed through 50.00 ml of the absorbing solution. The solution was treated with potassium permanganate and the formaldehyde formed was allowed to react with fuchsinsulphurous acid to give 90.00 ml of a coloured solution. In determining by the duplication method, before the colours were equalized, to the solution of the reagents there was added 4.50 ml of the standard solution and the volume was made up to 90 ml.

Determine the methanol concentration in the air (in mg/litre and per cent by volume) and find its excess over the permissible limit (50 mg/litre).

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. In what units is the molar extinction coefficient (molar absorptivity) measured?

(a) cm^{-1} . (b) moles/ cm^2 . (c) cm^2/mole . (d) moles. (e) It is a dimensionless quantity.

2. How does the optical density of a solution depend on its pH?

(a) Decreases with increasing pH.

(b) The character of the change depends on the nature of the coloured solution and temperature.

(c) With increasing pH the optical density first increases and then falls off.

(d) Drops with decreasing pH.

(e) With increase of pH the optical density first drops and then rises.

3. Which of the graphs given in Fig. 5 expresses the correct relation between the concentration and the layer thickness of a solution at constant D and different molar absorptivities ($\epsilon_2 > \epsilon_1$)?

4. What are the advantages and limitations of the duplication method as compared with the equalization method?

(a) It is faster, requires no conformity to the Bouguer-Lambert-Beer law but is less accurate.

(b) It is slower but more accurate.

(c) It makes it possible to carry out measurements in

the ultraviolet region of the spectrum, which cannot be done by means of the equalization method.

(d) It permits carrying out colorimetric analysis immediately after the formation of a colour, whereas the equalization method requires that the colour mature completely.

(e) No special advantages are offered by the duplication method.

5. The copper ion together with dithizone (molecular weight 256) forms a red-brown complex containing two particles of the reagent added per one copper ion. The optical

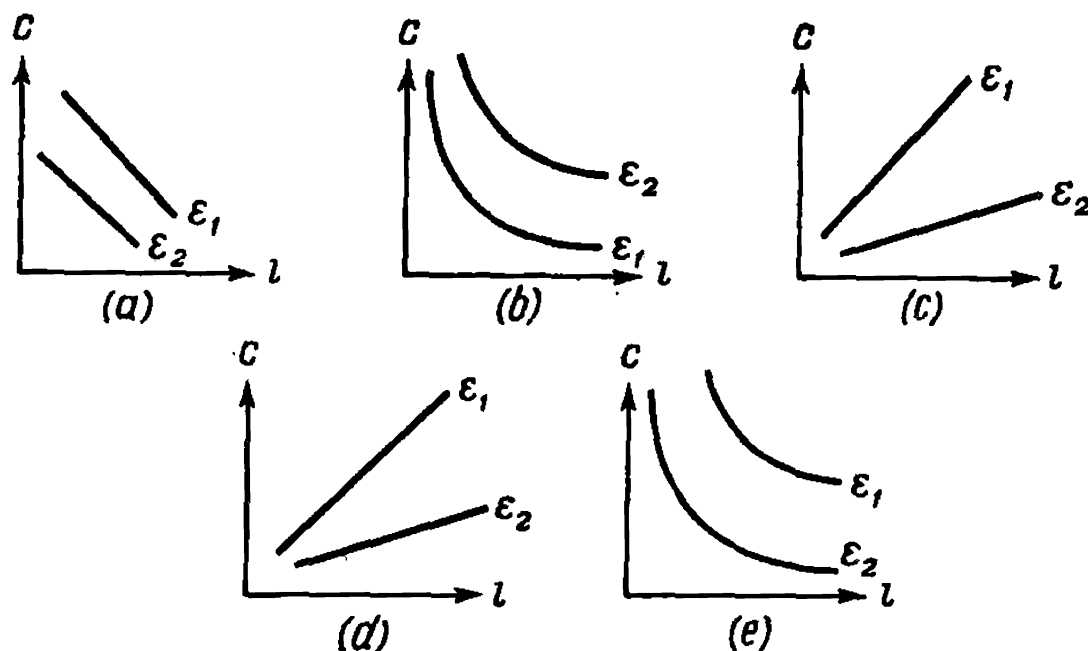


Figure 5

density of a solution containing 0.001 $\mu\text{g/ml}$ of copper in a cuvette 2 cm thick is 0.75. Which of the formulas given below can be used to calculate the molar extinction coefficient (molar absorptivity) of the complex?

(a) The data given are insufficient for the calculation to be made.

$$(b) \quad \epsilon = \frac{0.75}{10^{-3} \times 10^{-6} \times 10^3 \times 2} = 3.75 \times 10^5.$$

$$(c) \quad \epsilon = 0.75 \times 10^{-3} \times 10^{-6} \times 10^3 \times 2 = 1.5 \times 10^{-6}.$$

$$(d) \quad \epsilon = \frac{0.75 \times 64}{10^{-3} \times 10^{-6} \times 10^3 \times 2} = 2.4 \times 10^7.$$

$$(e) \quad \epsilon = \frac{0.75 \times 64}{10^{-3} \times 10^{-6} \times 10^3 \times 596 \times 2} = 4 \times 10^4.$$

6. In a determination of copper in a metal by the duplication method, after a sample of the metal weighing 0.5 g was dissolved and appropriately treated, 50 ml of a coloured ammonia solution was obtained. To equalize the colours, to the solution containing ammonia there was added 5.5 ml of a standard solution containing 0.5 mg/ml of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (molecular weight 250) and the solution was diluted to 50 ml. Which of the formulas listed below should be used to determine the percentage content of copper in the metal?

$$(a) \text{ Cu, per cent} = \frac{5.5 \times 0.5 \times 100}{0.5 \times 64} = 8.6.$$

$$(b) \text{ Cu, per cent} = \frac{0.5 \times 10^{-3} \times 50 \times 64 \times 100}{250 \times 0.5} = 1.28.$$

$$(c) \text{ Cu, per cent} = \frac{0.5 \times 5.5 \times 64}{250 \times 0.5} = 1.4.$$

$$(d) \text{ Cu, per cent} = \frac{0.5 \times 10^{-3} \times 5.5 \times 64 \times 100}{250 \times 0.5} = 0.14.$$

(e) The data given are insufficient. The density of the standard solution must also be known.

7. Which of the equations listed below gives the correct relation between the transmittance T , the optical density D , the concentration C , the molar extinction coefficient (molar absorptivity) ϵ and the layer thickness l ?

$$(a) T = -\log \frac{1}{D}.$$

$$(b) T = -\log D.$$

$$(c) \log 1/T = \epsilon l C.$$

$$(d) \log T = \epsilon l C.$$

$$(e) T = -\epsilon C l.$$

$$(f) \epsilon = D/C l.$$

$$(g) T = \epsilon C l.$$

$$(h) T \times 10^D = 1.$$

$$(i) D = \log T.$$

8. Which of the equations listed below reflects correctly the relations that exist between the variables if the Bouguer-Lambert-Beer law is obeyed?

(a) At $l = \text{const}$, if $C_1 < C_2 < C_3$, then

$$\frac{D_1}{\epsilon_1} > \frac{D_2}{\epsilon_2} > \frac{D_3}{\epsilon_3}$$

(b) If $C_1 < C_2 < C_3$, then

$$\frac{\epsilon_1 l_1}{D_1} < \frac{\epsilon_2 l_2}{D_2} < \frac{\epsilon_3 l_3}{D_3}$$

(c) At $l = \text{const}$, $\epsilon = \text{const}$ and $I_0 = \text{const}$, if $C_1 > C_2 > C_3$, then

$$I'_t < I''_t < I'''_t$$

(d) At $l = \text{const}$, $\epsilon = \text{const}$, and $I_0 = \text{const}$, if $C_1 > C_2 > C_3$, then

$$I'_t > I''_t > I'''_t$$

(e) At $\epsilon = \text{const}$ and $D = \text{const}$

$$\frac{C_1}{l_1} = \frac{C_2}{l_2} = \frac{C_3}{l_3}$$

(f) If $C_1 < C_2 < C_3$, then

$$\frac{\epsilon_1 l_1}{D_1} > \frac{\epsilon_2 l_2}{D_2} > \frac{\epsilon_3 l_3}{D_3}$$

(g) At $l = \text{const}$, if $C_1 < C_2 < C_3$, then

$$\frac{D_1}{\epsilon_1} < \frac{D_2}{\epsilon_2} < \frac{D_3}{\epsilon_3}$$

9. Indicate the conditions in which one could use, for a colorimetric analysis, the reactions, for which the time dependence of optical density is expressed by the graphs given in Fig. 6.

(1) Reactions for which this dependence is observed may be employed for analytical purposes after a definite time of colour maturing.

(2) Reactions for which this dependence is observed may be used immediately after the formation of a colour.

(3) Such a graph is most characteristic of colorimetric reactions. For analytical purposes, use is made of the colour intensity in a definite time interval.

(4) Reactions for which such a time dependence of optical density is observed cannot be used for analytical purposes.

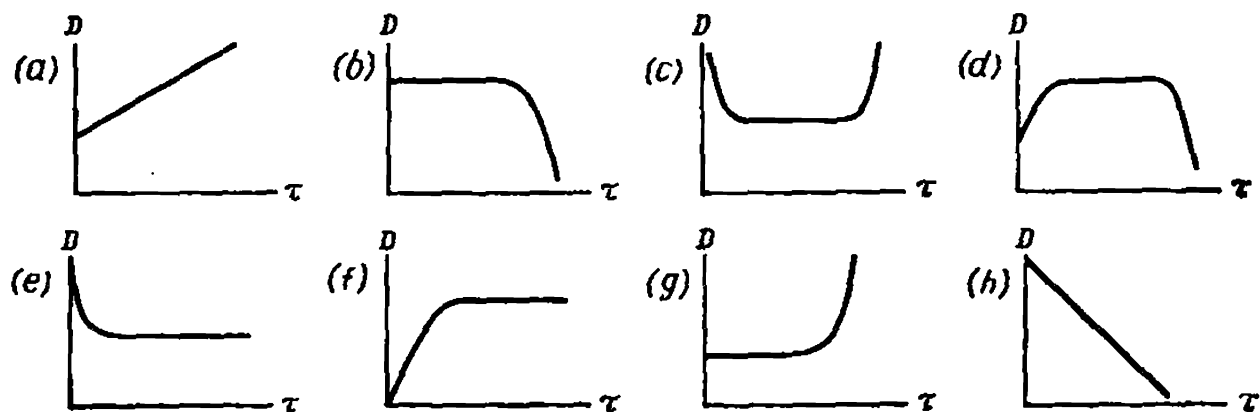


Figure 6

(5) Such a plot of optical density versus time is not realistic, it cannot actually be obtained.

10. Find under A the factors that are responsible for deviations from the Bouguer-Lambert-Beer law and under B the conditions in which this effect can be compensated.

A

- (a) The change of the concentration of hydroxyl ions.
- (b) The change of the oxygen concentration in the air.
- (c) The difference in the time the coloured solution is matured.
- (d) The change in the concentration of the reagents added.
- (e) The change in the concentration of CO_2 in the air.
- (f) The change of the temperature during the experiments.
- (g) The change of the atmospheric pressure.
- (h) The change of the air humidity.
- (i) The change in the concentration of the substance being determined.

B

- (1) To compensate this effect it is necessary to conduct colorimetric analysis during the time when the optical density does not vary with time.

(2) The colorimetric analysis must be carried out at constant concentration of oxygen and CO_2 in the air.

(3) The colorimetric analysis should always be conducted in a neutral medium ($\text{pH} = 7$).

(4) The concentration of all the reagents must be kept constant.

(5) The colorimetric analysis must always be carried out at room temperature maintained constant within 3 to 5 degrees.

(6) The temperature of the colour-forming reagent must be kept strictly constant within tenths of a degree.

(7) The colorimetric analysis must be carried out at a definite pH value at which the maximal value of optical density is attained and the optical density depends little on the variation of pH.

(8) The colorimetric analysis should be carried out immediately after the colour has been formed.

(9) The colorimetric analysis should be conducted in the atmosphere of clean air with its pressure being kept constant.

(10) The colorimetric analysis should be conducted in the regions of concentrations of the unknown substance where a direct proportionality between the optical density and the concentration is maintained. This is not necessarily important, for all methods of colorimetric analysis.

(11) The colorimetric analysis should always be conducted in the atmosphere of dry air.

(12) The conformity to the Bouguer-Lambert-Beer law is not practically affected by this factor.

Photometry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. In a photometric determination of titanium with chromotropic acid, in a solution containing $0.45 \mu\text{g}$ of titanium in 1 ml , in a cell 5 cm in length the galvanometer deflection was $90 \mu\text{A}$. For an incident beam of light the deflection on the galvanometer scale was $155 \mu\text{A}$.

Determine the molar extinction coefficient (molar absorptivity) of a coloured compound containing a molecule of chromotropic acid per titanium atom.

Solution: To solve the problem we make use of the Bouguer-Lambert-Beer equation:

$$I_t = I_0 10^{-\epsilon l C} \quad \text{or} \quad \log I_0 - \log I_t = \epsilon l C$$

Now we calculate the concentration of titanium (in moles per litre):

$$C = \frac{0.45 \times 10^{-6} \times 10^3}{47.9} = 0.94 \times 10^{-5}$$

From the equation given above we obtain:

$$\epsilon = \frac{\log I_0 - \log I_t}{l C} = \frac{\log 155 - \log 90}{5 \times 0.94 \times 10^{-5}} = \frac{2.192 - 1.955}{4.7 \times 10^{-5}} = 5 \times 10^3$$

Example 2. The molar extinction coefficient of a beryllium-acetylacetone complex in chloroform is $31,600$ for a wavelength of 295 nm .

What is the minimum percentage content of beryllium that can be determined in a 1-g sample dissolved in 50 ml , in a cell 5 cm in length, assuming that the minimum reading on the optical density (absorbance) scale of a photoelectric colorimeter is 0.025 ? The coloured compound contains a molecule of acetylacetone per beryllium atom.

Solution: Using the Bouguer-Lambert-Beer law, we get:

$$\log \frac{I_0}{I_t} = D = 0.025 = 31,600 \times 5C$$

$$C = \frac{0.025}{5 \times 31,600} = 1.58 \times 10^{-7} \text{ mole/litre}$$

Now we calculate the percentage content of beryllium (in g/50 ml):

$$\frac{1.58 \times 10^{-7} \times 9.01 \times 50}{1000} = 7.15 \times 10^{-8}$$

Hence the percentage of beryllium is

$$\frac{7.15 \times 10^{-8} \times 10^2}{1} = 7.15 \times 10^{-6}$$

Example 3. In a single-beam photoelectric colorimeter (absorptiometer), for an incident beam of light the reading on the galvanometer scale was 100 divisions. For a standard 0.00500M solution of a complex of copper and excess ammonia the galvanometer reading was 85.8 divisions.

Find the concentration of copper (in $\mu\text{g/ml}$) in the solution if the galvanometer scale reading for it is 93.5 divisions. Estimate the accuracy of the determination if the precision of the reading on the galvanometer scale is 0.5 division.

Solution. We set up two equations according to the Bouguer-Lambert-Beer law, one for the standard solution:

$$e l 0.005 = \log 100 - \log 85.8 = 2 - 1.933 = 0.067$$

and the other for the unknown solution:

$$e l C_x = \log 100 - \log 93.5 = 2 - 1.971 = 0.029$$

Dividing these equations, one by the other, we get:

$$\frac{0.067}{0.029} = \frac{0.00500}{C_x}; \quad C_x = \frac{0.00500 \times 0.029}{0.067} = 0.00217 \text{ mole/litre}$$

We calculate the concentration of copper (in $\mu\text{g/ml}$):

$$\frac{0.00217 \times 63.5 \times 10^6}{10^3} = 137 \mu\text{g/ml}$$

Now we calculate the possible error by the method of limits. The minimum concentration corresponds to the

minimum possible value of the reading for the standard solution and the maximum possible reading for the unknown solution; for the maximum concentration the situation is reverse. Hence we obtain a series of calculations:

(a) for the minimum concentration value

$$\frac{\log 100 - \log 94}{\log 100 - \log 85.3} = \frac{2 - 1.974}{2 - 1.930} = \frac{0.026}{0.070} = 0.371$$

$$C_{\min} = \frac{0.005 \times 0.371 \times 63.5 \times 10^6}{10^3} = 118 \mu\text{g/ml}$$

(b) for the maximum concentration value

$$\frac{\log 100 - \log 93}{\log 100 - \log 86.3} = \frac{2 - 1.968}{2 - 1.936} = \frac{0.032}{0.064} = 0.500$$

$$C_{\max} = \frac{0.005 \times 0.500 \times 63.5 \times 10^6}{10^3} = 156 \mu\text{g/ml}$$

Example 4. In a photometric determination of iron in water according to the reaction with sulphosalicylic acid the following data were obtained for standard solutions:

| | | | | | | |
|---------------------------------|-----|------|------|------|------|------|
| Content of iron, per cent . . . | 0 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 |
| Galvanometer scale reading . . | 100 | 87.5 | 77.5 | 68.5 | 59.0 | 52.5 |

Plot calibration graphs in the Δ vs. C and D vs. C coordinate systems. Derive an equation for the second graph and determine the content of iron graphically and by calculation if the galvanometer scale reading is 71.5. Using the D vs. C graph, estimate the accuracy of the determination if the precision of the scale reading is 0.5 division.

Solution: We calculate the optical densities from the following data:

| | | | | | | |
|---------------------------------|-----|-------|-------|-------|-------|-------|
| Content of iron, per cent . . . | 0 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 |
| Deflection | 100 | 87.5 | 77.5 | 68.5 | 59.0 | 52.5 |
| Deflection logarithm | 2 | 1.942 | 1.890 | 1.836 | 1.770 | 1.720 |
| Optical density | — | 0.058 | 0.110 | 0.164 | 0.230 | 0.280 |

Using these data, we plot calibration graphs (see Fig. 7). From the Δ vs. C graph (1) we find the value of the unknown concentration corresponding to the scale reading 71.5. This concentration is equal to 0.270. Using the same data, we plot a graph in the D vs. C coordinate system (2).

We now calculate the equation for the resulting curve by using the method of selected points. The point chosen is the last point for which the reading at $C = 0.5$ per cent

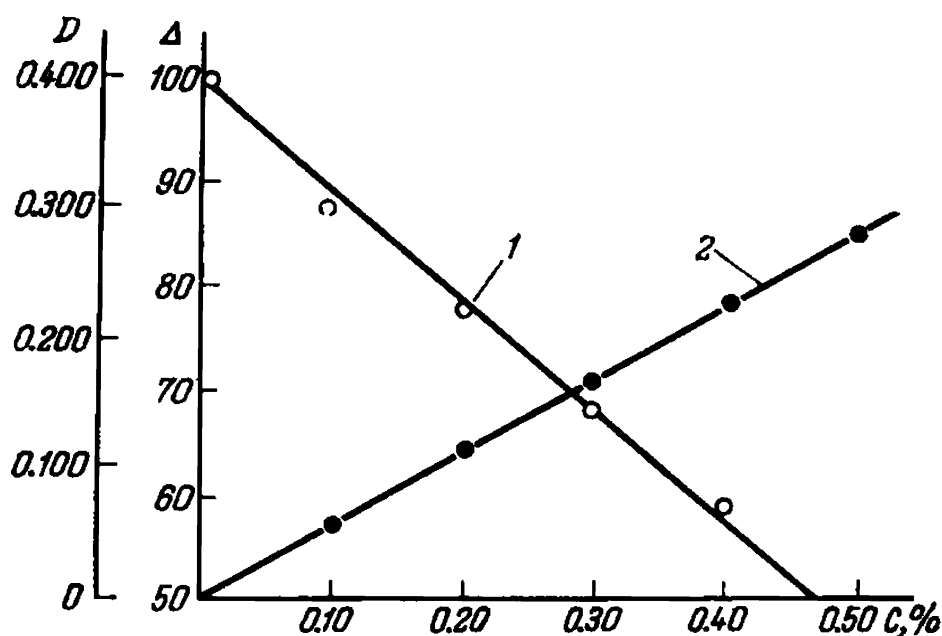


Figure 7

is 0.280. Hence the coefficient in the equation representing the relationship between D and C will be

$$k = \frac{0.280}{0.5} = 0.560$$

The equations for the sought-for dependence have the following form:

$$D = 0.560 C \text{ and } C = 1.79 \cdot D$$

where C is the percentage content of iron.

Checking the derived equation, we have:

| | | | | | |
|------------------------------------|--------|--------|--------|--------|--------|
| D | 0.058 | 0.110 | 0.164 | 0.230 | 0.280 |
| C_{exp} | 0.100 | 0.200 | 0.300 | 0.400 | 0.500 |
| C_{cal} | 0.103 | 0.196 | 0.292 | 0.405 | 0.498 |
| ΔC | +0.003 | -0.004 | -0.008 | +0.005 | -0.002 |
| $\Delta C^2 \times 10^6$ | 9 | 16 | 64 | 25 | 4 |

So the rms (root-mean-square) error is $118 \times 10^{-4}/(5-1) = 0.005$. It lies within the precision limits of the reading and, hence, the derived equation does reflect satisfactorily the relation between optical density and concentration.

We calculate D for $\Delta = 71.5$; $D = \log 100 - \log 71.5 = 2 - 1.854 = 0.146$. For this value of D we find, using the graph, the value of the concentration, $C_x = 0.258$. According to the calculating equation given above $C = 1.79D = 1.79 \times 0.146 = 0.261$ per cent.

Using the equation and the D vs. C graph, we estimate the accuracy of the reading at the given concentrations. Taking into account that the reading accuracy is 0.5 division, we obtain the limiting values of the readings on the galvanometer scale: the minimum value is 71 and the maximum, 72. Accordingly, $D_{\min} = 0.142$ and $D_{\max} = 0.148$. For these values we find from the graph: $C_{\min} = 0.252$ and $C_{\max} = 0.262$. Hence the positive and negative errors of the determination are different:

$$C = 0.258^{+0.004}_{-0.006}$$

From the equation we get:

$$C_{\min} = 1.79 \times 0.142 = 0.254$$

$$C_{\max} = 1.79 \times 0.148 = 0.265$$

These values are close enough.

Example 5. Determine the composition of a complex of nickel and xylenol orange from the following values of the optical density obtained by adding the reagent in portions of increasing concentration to equal volumes of a solution of nickel with a constant concentration of nickel of 1×10^{-5} g-ion/litre:

| | | | | | |
|---|-------|-------|-------|-------|-------|
| Concentration of reagent, $C \times 10^5$, mole/litre | 0.12 | 0.16 | 0.20 | 0.40 | 0.60 |
| Optical density | 0.040 | 0.050 | 0.065 | 0.130 | 0.200 |
| Concentration of reagent, $C \times 10^5$, mole/litre | 0.80 | 1.00 | 1.20 | 1.48 | 1.80 |
| Optical density | 0.270 | 0.315 | 0.360 | 0.365 | 0.370 |

Solution: Using the data given above, we construct a plot of the optical density against the concentration of xylenol orange (see Fig. 8). Eliminating the point near the break point of the straight lines (for $C = 1.0 \times 10^{-5}$), we get an

intersection of the straight lines at a xylenol orange concentration of 1.04×10^{-5} . Hence, the composition of the complex will be $[\text{Ni}] : [\text{R}] = 1 : 1$.

Example 6. Calculate the dissociation constant of a reagent HR if at $\text{pH} = 7.33$ the optical density D_{mix} is equal to 0.442. In an acidic medium at $\text{pH} < 2$ the optical density D_{HR} is 0.017, and in an alkaline medium at $\text{pH} > 11$ the optical density D_{R} is 0.705.

Solution: We make use of the equation

$$K_{\text{HR}} = \frac{D_{\text{mix}} - D_{\text{HR}}}{D_{\text{R}} - D_{\text{mix}}} [\text{H}^+]$$

Substituting the values given above, we get:

$$\text{pH} = 7.33 \quad [\text{H}^+] = 10^{-7.33} = 4.67 \times 10^{-8}$$

$$K_{\text{HR}} = \frac{0.442 - 0.017}{0.705 - 0.442} \times 4.67 \times 10^{-8} = 7.35 \times 10^{-8}$$

Example 7. Calculate the sensitivity of a determination (the determinable minimum) of copper according to the reaction with diethyldithiocarbamate (the composition of the complex is CuR) at $\lambda = 436 \text{ nm}$ if the thickness of the absorbing layer is $l = 5 \text{ cm}$ and the minimum volume of the coloured solution $V = 25 \text{ ml}$. The molar extinction coefficient of the coloured compound is $\epsilon_{436} = 12.8 \times 10^3$. The minimum value of optical density measured by an instrument is 0.005.

Solution: We make use of the equation

$$\begin{aligned} m &= \frac{D_{\text{min}} S n A \cdot 10^3}{\epsilon_{436}} = \frac{D_{\text{min}} V n A \cdot 10^3}{\epsilon_{436} l} = \\ &= \frac{5 \times 10^{-3} \times 25 \times 1 \times 63.54 \times 10^3}{12.8 \times 10^3 \times 5} = 0.125 \text{ } \mu\text{g} \end{aligned}$$

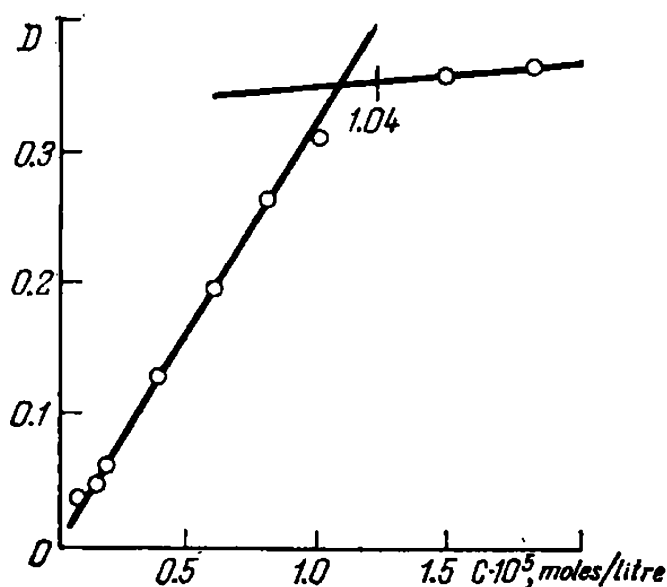


Figure 8

2. MULTIVARIANT PROBLEMS

1. Determine the parameter denoted by x in Table 11 in terms of the units indicated by using the Bouguer-Lambert-Beer equation.

2. Using the data given in Table 12, determine the concentrations of the solutions in terms of the units indicated.

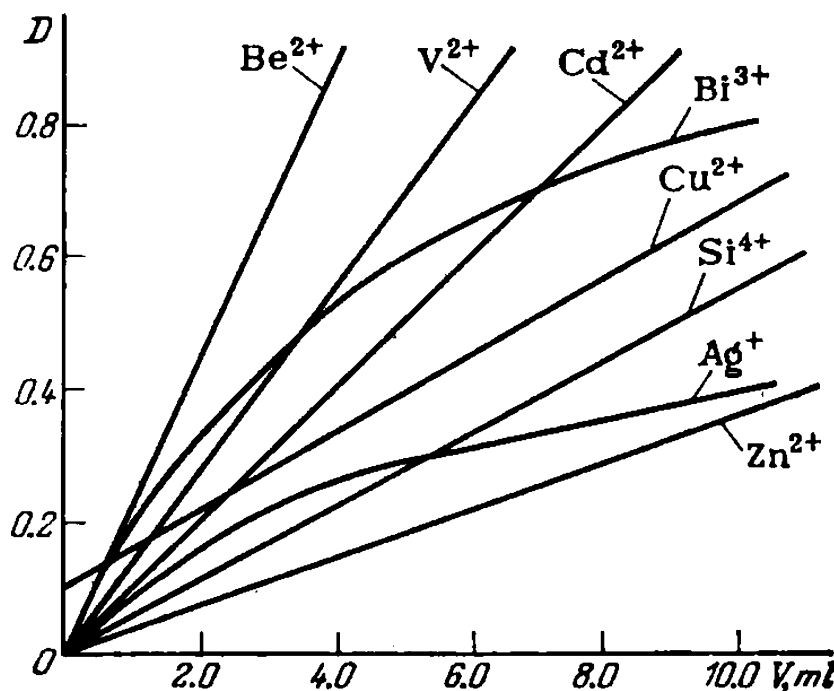


Figure 9

3. Determine the concentrations of the unknown solutions under the given conditions (see Table 13) by using the calibration graph of Fig. 9.

3. PROBLEMS

SECTION A

1. In plotting the calibration graph for determining copper in a solution the following data were obtained on a single-beam photometer (absorptiometer):

| | | | | | | | |
|-----------------------------|-----------|----|------|------|------|------|------|
| Content of copper, mg/litre | . . . | 0 | 0.1 | 0.2 | 0.5 | 0.75 | 1.0 |
| Galvanometer reading | | 80 | 67.5 | 57.0 | 34.5 | 28.5 | 15.0 |

Plot calibration graphs in the following systems of coordinates: the optical density versus the concentration of copper

TABLE 11

| Vari- ant | Ion or subst- ance being determined | Reaction by which coloured compound is formed | Wave- length, nm | ϵ | Layer thickness, cm | Current, in scale divi- sions | | Concentration | Optical density |
|--------------|---|---|------------------------|------------|---------------------------|-------------------------------------|--------------------------|------------------------------------|--------------------|
| | | | | | | initial | after absorp- tion | | |
| I | MnO ₄ ⁻ | Intrinsic colour | 546 | 2,420 | 1.00 | — | — | 0.0150 g/100 ml | x |
| II | Cu ²⁺ | With dithizone CuR ₂ in CCl ₄ | 620 | 35,000 | 1.00 | 100 | 75 | x mg/ml | |
| III | Pb ²⁺ | With dethizone PbR ₂ in CHCl ₃ | 520 | 70,000 | 5.00 | 80 | x | 1.05 μ g/ml | |
| IV | Fe ³⁺ | With orthophe- nanthraline FeR ₃ | 490 | x | 2.00 | 150 | 95 | 0.52 μ g/ml | |
| V | Al ³⁺ | With oxyquino- line AlR ₃ | 390 | 6,700 | x | — | — | 2.5×10^{-4} mole/litre | 0.836 |
| VI | Ge ⁴⁺ | With phenylfluoro- ne GeR ₂ | 510 | 10,000 | 5.00 | 200 | 165 | x μ g/ml | |
| VII | Quinoline | Intrinsic colour | 275 | 4,500 | 2.00 | — | — | 3 mg/litre | x |
| VIII | Azobenzene | Intrinsic colour | 438 | 1,100 | 5.00 | — | — | x mg/ml | 0.356 |

TABLE 12

| Vari- ant | Ion to be determi- ned | Reaction by which coloured com- pound is formed | Initial cur- rent, μA | Standard solution | | | Unknown solution | | |
|--------------|------------------------------|---|---|---|--------------------------------|--------------------------------|--|--------------------------------|--------------------------------|
| | | | | concentration | layer thick- ness, cm | cur- rent, μA | concentration | layer thick- ness, cm | cur- rent, μA |
| I | Mg^{2+} | With eriochro- me black T | 100 | 0.100 g MgCl_2 in 250 ml of solu- tion | 2.00 | 60 | Mg (in per cent) in a 0.2-g mi- neral sample in 50 ml of solu- tion | 3.00 | 90 |
| II | $\text{Cr}_2\text{O}_7^{2-}$ | Intrinsic colour | 90 | A solution of $\text{K}_2\text{Cr}_2\text{O}_7$ with a titre of 0.00450 g/ml with respect to Fe(II) | 1.00 | 83.4 | Cr (in mg/ml) | 1.00 | 75.2 |
| III | MoO_4^{2-} | With dithiol | 75 | A 0.1-g sample of steel CO contain- ing 0.750 per cent Mo in 25 ml of solution | 5.00 | 64.8 | Mo (in per cent) in a 0.2-g samp- le of steel in 25 ml of solu- tion | 2.00 | 59.6 |
| IV | Ni^{2+} | With dimethyl- glyoxime | 100 | 0.250 g $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 1 litre of solu- tion | 1.00 | 53.2 | Ni (in mg/ml) | 5.00 | 73.4 |

Table 12, continued

| Vari- ant | Ion to be determi- ned | Reaction by which coloured com- pound is formed | Initial cur- rent, μ A | Standard solution | | | Unknown solution | | |
|--------------|------------------------------|---|-------------------------------------|--|--------------------------------|--------------------------|--|--------------------------------|--------------------------|
| | | | | concentration | layer thick- ness, cm | cur- rent, μ A | concentration | layer thick- ness, cm | cur- rent, μ A |
| V | Pb ²⁺ | With dithizone | 100 | 2.5 mg PbO ₂ in 100 ml of solu- tion | 5.00 | 74.8 | Pb (in mg/litre) | 5.00 | 92.6 |
| VI | Sb ³⁺ | With methyl violet | 100 | 2.56 mg Sb in 50 ml of solution | 0.5 | 82.3 | Sb ₂ O ₃ (in per cent) in a 0.5-g mineral sample in 100 ml of solution | 2.5 | 74.6 |
| VII | Fe ³⁺ | With KSCN | 90 | A 0.00186N solu- tion of FeCl ₂ | 1.0 | 54.6 | Fe (in μ g/ml) | 5.0 | 83.4 |
| VIII | Cu ²⁺ | With ammonia | 75 | A 0.1-g sample of an alloy contain- ing 5.26 per cent Cu in 100 ml of solution | 2.5 | 51.4 | Cu (in per cent) in a 0.2-g samp- le of an alloy in 250 ml of solution | 5.0 | 63.2 |

TABLE 13

| Variant | Ion to be determined | Reaction by which coloured compound is formed | Concentration of standard solution | Unknown solution | |
|---------|----------------------|---|---|------------------|--|
| | | | | optical density | concentration |
| I | Be ²⁺ | With eriochromeyanine | 0.150 g BeSO ₄ ·4H ₂ O in 250 ml of solution | 0.55 | Be (in mg/ml) |
| II | V ³⁺ | With phosphotungstic acid | 0.25 mg V ₂ O ₃ | 0.84 | V (in mg/ml) |
| III | Cd ²⁺ | With dithizone | 0.550 g Cd(NO ₃) ₂ ·4H ₂ O in 50 ml of solution | 0.14 | Cd (in g/litre) |
| IV | Bi ³⁺ | With thiourea | 0.100 g Bi ₂ O ₃ in 200 ml of solution | 0.31 | Bi (in per cent) in a 0.2-g sample of an alloy in 100 ml of solution |
| V | Cu ²⁺ | With dithizone | 0.100 g of an alloy containing 3.25 per cent Cu in 250 ml of solution | 0.52 | CuO (in mg/50 ml) |
| VI | Si ⁴⁺ | With ammonium molybdate | 0.250 g SiO ₂ in 0.5 litre of solution | 0.37 | Si (in per cent) in a 1-g sample of steel in 100 ml of solution |
| VII | Ag ⁺ | With diethylaminobenzylidenetriphenylamine | 5.5 mg AgNO ₃ in 25 ml of solution | 0.31 | Ag (in mg/litre) |
| VIII | Zn ²⁺ | With dithizone | 0.150 g ZnSO ₄ ·7H ₂ O in 0.5 litre of solution | 0.22 | ZnO (in mg/100 ml) |

and the galvanometer deflection versus the concentration of copper, and determine the copper content of the unknown solution if the galvanometer deflection is 45.5 divisions.

2. To determine phosphorus in steel by the dark-blue colour of a reduced phosphomolybdic complex on a photometer the following data were obtained for standard samples of steel CO:

| | | | | | |
|---|-------|-------|-------|-------|-------|
| Content of phosphorus in steel CO, per cent | 0.011 | 0.024 | 0.031 | 0.040 | 0.055 |
| Photometer reading in terms of diaphragm scale divisions . . | 48 | 29 | 19 | 12 | 5 |

Determine the percentage content of phosphorus in the unknown sample if the reading on the diaphragm scale is 24 divisions.

3. To determine iron in industrial water 25 ml of a coloured solution was obtained from 100 ml of the water after evaporation and treatment with *o*-phenanthroline. The optical density of this solution with a layer thickness of 1 cm was found to be 0.460.

Determine the iron content of industrial water (in mg/litre) if the molar extinction coefficient of this coloured compound is 1100.

4. To determine molybdenum in steel the volumes indicated below were taken from a standard solution containing 0.1124 g of $\text{H}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in 100 ml of solution, treated with phenylhydrazine and diluted with water to 100 ml. The following values of the optical density of the solutions were obtained:

| | | | | | |
|----------------------------|------|------|------|------|------|
| Volume taken, ml | 2 | 4 | 6 | 8 | 10 |
| Optical density | 0.05 | 0.11 | 0.16 | 0.21 | 0.25 |

A 1.2-g sample of steel was dissolved in acid and diluted with water to 50 ml. After appropriate treatment 5 ml of this solution gave 100 ml of a coloured solution. The optical density of the solution was found to be equal to 0.12.

Determine the percentage content of molybdenum in the steel.

5. To determine copper in a nonferrous alloy a sample weighing 0.325 g was dissolved and treated with ammonia

and 250 ml of a coloured solution was obtained, whose optical density in a cell 2 cm in length was 0.254.

Determine the percentage content of copper in the alloy given that the molar extinction coefficient of copper ammoniate is 423.

6. Calculate the molar extinction coefficient of copper if the optical density of a solution containing 0.24 mg of copper in 250 ml is 0.14 in a cell 2 cm in length.

7. A 1-g sample of a tin-containing metal was dissolved in acid and the resulting solution diluted with water to 100 ml. Five samples of 10.0 ml each were taken from the solution and treated with dithiol. As a result, coloured solutions were obtained, 25 ml each, whose optical densities were 0.32, 0.35, 0.30, 0.31, and 0.33.

A standard solution was made by dissolving 1 g of a metal containing 4.56 per cent of tin and by treating it under the same conditions. The optical densities of the resulting solutions were 0.20, 0.23, 0.23, 0.21, and 0.24.

Determine the percentage content of tin in the metal and the error of the determination.

8. To plot a calibration graph in determining vanadium, use was made of four standard samples of steel CO containing the following amounts of vanadium: I—0.15, II—0.33, III—0.58, IV—0.72 per cent.

Samples of steel CO weighing 0.5 g each were dissolved and after treatment with hydrogen peroxide coloured solutions were obtained, each having a volume of 50 ml. When these solutions (I-IV) were analysed photometrically on a single-beam photoelectric colorimeter, the galvanometer scale showed the following deflections: background—100; I—79, II—61, III—41.5, IV—34.5.

Determine the percentage content of vanadium in the unknown sample if the deflection on the galvanometer scale was 52.5 divisions for this sample under the same conditions.

9. A reference solution was prepared by dissolving 0.258 g of lead nitrate in 250 ml of water. The treatment of 5 ml of the solution with dithizone resulted in 50 ml of a coloured solution. The coloured compound was extracted with 10 ml of chloroform and the optical density of the chloroform layer was found to be 0.35.

A 1-g sample of the alloy being analysed was dissolved in acid and the resulting solution was diluted with water to 100 ml. When 10 ml of this solution was treated with dithizone, 25 ml of a coloured solution was obtained. The coloured compound was extracted with 10 ml of chloroform and the optical density of the chloroform layer in the same cuvette was found to be 0.14.

Determine the percentage content of lead in the alloy.

10. To plot a calibration graph in determining manganese, six samples of a 0.0125*N* solution of KMnO_4 weighing 2.5, 5.0, 7.5, 10.0, 12.5, and 15.0 ml were taken and diluted with water to 100 ml. The deflection on the galvanometer scale in a single-beam photoelectric colorimeter was 80 divisions for the background; for the solutions indicated the galvanometer scale showed 72.5, 64.5, 59.0, 62.5, 47.0, and 42.5 divisions.

A 0.5-g sample of steel was dissolved and after the manganese was oxidized the solution was diluted with water to 50 ml. The deflection on the galvanometer scale was 55.5 divisions for the coloured solution under the same conditions.

Determine the percentage content of manganese in the steel.

11. In investigating a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ the galvanometer deflection on a single-beam photometer was 75 scale divisions. After 1 ml of a standard 0.015*N* solution of potassium dichromate was added to a 5-ml cuvette the deflection was 65 scale divisions at constant layer thickness.

Determine the concentration of the unknown solution (in mg/ml) if the deflection on the galvanometer scale for the background is 100 divisions.

12. In a photometric titration, on a single-beam photoelectric colorimeter, of 10 ml of a KMnO_4 solution with a solution of NaNO_2 , whose titre was 0.0015 g/ml, the following data were obtained:

| | | | | | | | |
|--|----|------|------|------|------|------|------|
| Volume of NaNO_2 solution, ml | 0 | 0.5 | 1.0 | 1.25 | 1.5 | 1.75 | 2.0 |
| Galvanometer reading | 50 | 59.0 | 66.5 | 75.0 | 77.5 | 77.0 | 78.0 |

The deflection for the background was 80 scale divisions.

Determine the normality of the unknown solution.

13. To determine the aluminium impurity in magnesium silicate a 0.2-g sample of magnesium silicate was fused with

soda and after treating with acid the volume of the solution was made up to 200 ml by adding water. To prepare a solution to be analysed colorimetrically a 20-ml aliquot was brought to 50 ml after aluminon was added to it. The optical densities of this solution and the solution to which 5 ml of a $5 \times 10^{-4} M$ solution of $AlCl_3$ was added, measured relative to distilled water in a cell 2 cm in length, were 0.25 and 0.55, respectively.

Compute the percentage of aluminium in anhydrous magnesium silicate if the silicate is known to contain 5 per cent of water.

14. To plot a calibration curve for the determination of nickel on a single-beam photometer 550 mg of nickel sulphate containing 15.5 per cent of crystallization and hygroscopic water was dissolved in 250 ml of water. After dimethylglyoxime and other reagents were added the following volumes of the solution were made up to 25 ml with water and analysed photometrically three times. The results obtained were as follows:

| Volume of solution, ml . . | 0 | 2.5 | 5 | 7.5 | 10 | 12.5 | 15 |
|----------------------------|-----|-----|------|------|----|------|------|
| Galvanometer reading | | | | | | | |
| 1 | 100 | 89 | 80 | 71.5 | 63 | 56.5 | 49.5 |
| 2 | 98 | 90 | 78 | 70 | 63 | 55.5 | 50 |
| 3 | 100 | 89 | 79.5 | 72 | 64 | 56 | 49 |

Plot the calibration curve and derive the equation of a straight line.

A 0.75-g sample of the metal being analysed was dissolved in 25 ml of acid; 5 ml of the resulting solution after treatment with reagents was diluted with water to 50 ml. The galvanometer deflections for the solution obtained were 65, 66.5, 66, 65, and 65 scale divisions.

Determine the percentage content of nickel in the metal and the error of the determination.

15. To determine iron in waste water a 0.0586-g sample of pure iron oxide containing 2.5 per cent of hygroscopic water was dissolved in acid and the volume of the solution made up to 250 ml. To plot a calibration graph a solution of ammonium rhodanide was added to the following volumes of the resulting solution, and the solutions were diluted with water to 100 ml and analysed colorimetrically on a photometer with a diaphragm. The data obtained are as follows:

| | | | | | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|
| Volume of solution, ml | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| Diaphragm scale reading . . . | 17 | 31 | 42 | 51 | 58 | 64 |

A 2.5-l volume of waste water was evaporated to 50 ml and 15 ml of the solution was diluted with water to 25 ml after a solution of ammonium rhodanide was added to it. For the coloured solution obtained the reading on the diaphragm scale was 25 divisions.

Determine the iron content in the waste water (in g/m³).

16. To plot a calibration graph for the determination of phosphorus as a phosphomolybdic complex, a solution was prepared by dissolving 0.25 g of Na₂HPO₄ in 100 ml of water. After appropriate treatment the volumes of this solution indicated below were diluted with water to 25 ml. When they were analysed photometrically, the following results were obtained:

| | | | | | |
|-------------------------------------|------|------|------|------|------|
| Volume of standard solution, ml . . | 0.1 | 0.25 | 0.50 | 1.0 | 1.5 |
| Optical density | 0.06 | 0.10 | 0.13 | 0.22 | 0.31 |

A 0.50-g sample of a semiconducting metal was dissolved and after its treatment 100 ml of a slightly coloured solution was obtained. Its colour was then strengthened by adding to it 2 ml of the standard solution mentioned above; the optical density was found to be equal to 0.16.

Determine the percentage content of phosphorus in the sample.

17. A steel sample weighing 0.0532 g was dissolved in acid, the solution was treated with diethyldithiocarbamate and its volume made up to 100 ml. The solution was then analysed photometrically at 328 and 368 nm in a cell with a layer thickness of 2 cm. The results obtained were as follows: $D = 0.67$ at $\lambda = 328$ nm and $D = 0.45$ at $\lambda = 368$ nm.

Determine the percentage contents of nickel and cobalt in the steel if $\epsilon_{Ni} = 35,210$ and $\epsilon_{Co} = 3910$ at 328 nm and $\epsilon_{Ni} = 21,820$ and $\epsilon_{Co} = 14,340$ at 368 nm.

18. To plot a calibration graph for the determination of silicon over a wide range of concentrations use was made of three standard samples of silicon-containing steel: sample A—0.03 per cent Si, sample B—0.28 per cent Si, and sample C—1.35 per cent Si. These samples were used to prepare the mixtures indicated below, which were dissolved and coloured solutions were obtained, containing a silicomolybdic

complex and then diluted with water to 100 ml. After these solutions were analysed photometrically the following readings were obtained on the galvanometer scale of a single-beam photoelectric colorimeter:

| | | | | | | | | |
|---------------------------|------|------|------|------|------|------|-----|-----|
| Mixture | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Composition of mixture, g | | | | | | | | |
| A | 0.5 | 0.25 | — | — | — | — | 0.1 | — |
| B | — | 0.25 | 0.5 | 0.4 | 0.3 | 0.2 | — | — |
| C | — | — | — | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| Galvanometer reading . . | 95.5 | 76 | 60.5 | 42.5 | 27.5 | 22.5 | 15 | 9.5 |

The reading on the galvanometer scale for the background solution was 100 divisions.

A 0.4-g sample of steel was dissolved and after being treated as indicated above the volume of the solution was made up to 50 ml with water. In an analysis with a photoelectric colorimeter under the same conditions the reading on the galvanometer scale was 52.5 divisions.

Determine the percentage content of silicon in the steel.

19. Four standard solutions of an iron(II) salt were prepared, which contained 1.00, 1.05, 1.10, and 1.15 mg of iron. The optical densities of the coloured solutions with *o*-phenanthroline as measured with respect to the first solution were, respectively, 0.24, 0.51 and 0.75. The optical density of the unknown coloured solution measured under the same conditions was equal to 1.20.

Determine the iron content of the unknown solution (in mg) if the fifth part of the solution was used to prepare the coloured solution.

20. In determining bismuth in an alloy containing up to 0.02 per cent of bismuth use is made of the photometric reaction with thiourea.

Calculate the ratio of the optimal weight of the alloy samples (in grams) to the optimal final volume (in millilitres) of the solution being analysed photometrically if the molar absorptivity of the bismuth-thiourea complex $\text{Bi}[\text{SC}(\text{NH}_2)_2]_3$ is 35,000, the thickness of the absorbing layer $l = 5$ cm, and the optimal value of the optical density $D = 0.43$. Photometric analysis is carried out at $\lambda = 322$ nm; the molar extinction coefficient of the thiourea solution is 3000 at 322 nm.

21. To determine molybdenum by the reaction with dithiol the calibration graph must cover the range of optical densities from 0.15 to 1.50.

Find the weight of a sample of pure MoO_3 that should be dissolved in 25 ml of alkaline solution for the optical densities of the samples taken, 1 to 10 ml in volume, and diluted to 50 ml, to be 0.15 to 1.50 if the layer thickness in the cuvette is 1 cm and the molar absorptivity of the coloured solution is 1.3×10^4 .

22**. A 0.125-g sample of a semiconducting metal containing tellurium was dissolved and after the tellurium was reduced to the elemental state 100 ml of a coloured solution of tellurium sol was obtained. The optical density of this solution in a cell 1 cm in length was 0.175.

Determine the concentration of tellurium (in atoms/cm³) in the semiconducting metal if the molar absorptivity (molar extinction coefficient) of tellurium sol is 3.25×10^3 and the density of the semiconducting metal is 4.5 g/cm³.

23. To determine silicon in steels as a silicomolybdic complex a calibration graph was plotted for pure silicon dioxide. The data obtained on the optical density scale were as follows:

| | | | | | | |
|--|------|------|------|------|------|------|
| Content of silicon dioxide, mg/ml | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 | 1.20 |
| Optical density | 0.15 | 0.29 | 0.43 | 0.61 | 0.74 | 0.90 |

A 0.253-g sample of steel was dissolved in acid and after appropriate treatment 100 ml of a coloured solution of silicomolybdic acid was obtained, whose optical density was 0.56.

Find the percentage content of silicon in the steel.

24. Calculate the determinable minimum amount (in μg) of iron(III) according to the reaction with sulphosalicylic acid in ammonia solution if the thickness of the absorbing layer is 5 cm and the minimum volume of the coloured solution is 15 ml. The molar absorptivity of the complex equals 4000. The minimum optical density as measured by a photoelectric colorimeter is 0.01.

25. The molar absorptivity of a complex of iron and sulphosalicylic acid is 4000 at a wavelength of 416 nm.

Find the weight of a portion of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ that must be dissolved in 50 ml of water so that 5 ml of this solution

when subjected to appropriate treatment and diluted to 25 ml would give a coloured solution with an optical density of 1.5 in a cell 2 cm in length.

26. The molar absorptivity of a coloured complex of nickel and α -benzoyldioxime is 12,000 at a wavelength of 406 nm.

Determine the minimum concentration of nickel (in mg/ml) that can be determined photometrically in a cuvette 5 cm in length if the minimum optical density recorded by the instrument is 0.020.

27. A 1-g sample of a semiconducting metal was dissolved in 25 ml of acid and 5 ml of the resulting solution when subjected to appropriate treatment gave 10 ml of a coloured solution (the composition of the coloured solution is RbR). The coloured compound was extracted with 2 ml of chloroform and the chloroform extract was analysed photometrically in a cuvette with a layer thickness of 2 cm.

What molar absorptivity must the coloured compound exhibit for the optical density to be 0.020 at a concentration of lead of 2×10^{-5} per cent in the semiconducting metal chosen?

SECTION B

28. In a photometric examination of the solution in a dyeing vat after a hundred-fold dilution the following values of the optical density were obtained in a cuvette with a layer thickness of 5 cm at two wavelengths λ_1 and λ_2 : before dyeing $D_{\lambda_1} = 2.2$ and $D_{\lambda_2} = 1.6$; after dyeing $D_{\lambda_1} = 0.40$ and $D_{\lambda_2} = 0.25$.

Determine the degree of extraction of dyes from the vat if $\epsilon_{\lambda_1} = 3400$ and $\epsilon_{\lambda_2} = 1500$ for dye A and $\epsilon_{\lambda_1} = 1300$ and $\epsilon_{\lambda_2} = 2500$ for dye B.

29. The optical density of a 0.001M solution of potassium dichromate in a cuvette with a layer thickness of 1.0 cm is 1.15 at 410 nm and 0.11 at 675 nm. The corresponding values for a 0.05M solution of copper sulphate under the same conditions are 0.15 and 1.40.

A 4.45-g portion of a mixture containing both these salts was dissolved in 500 ml of water and when 10 ml of the resulting solution was diluted to 100 ml, a solution was

obtained, whose optical densities were found to be 2.40 and 0.65 at the indicated wavelengths, respectively.

Determine the contents of the salts in the mixture. What error would be introduced into these determinations if the optical densities of copper sulphate and potassium dichromate at 410 and 675 nm, respectively, were not taken into account?

30**. To provide a continuous photometric control of the content of NO_2 in the gases evolved in the production of nitric acid a calibration graph was plotted with the photometer readings against the amount of a 0.1*N* solution of KOH consumed.

| | | | | | |
|---|-----|------|------|------|------|
| Photometer reading, arbitrary units | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
| Volume of 0.1 <i>N</i> solution of KOH used, ml | 6.9 | 13.7 | 20.9 | 27.9 | 34.8 |

The KOH solution was used to titrate the nitric acid obtained by the reaction



from 5 litres of a gas containing NO_2 .

In the course of production control the following photometer readings were taken every 10 minutes during 2 hours:

| | | | | | | | |
|---|------|------|------|------|------|------|------|
| Time, min | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
| Photometer reading, arbitrary units | 0.33 | 0.34 | 0.45 | 0.50 | 0.50 | 0.40 | 0.30 |
| Time, min | 70 | 80 | 90 | 100 | 110 | 120 | |
| Photometer reading, arbitrary units | 0.28 | 0.28 | 0.28 | 0.35 | 0.40 | 0.45 | |

Determine the amount of NO_2 (in kg) that passed through a gas pipe if its cross-sectional area is 0.45 m^2 and the velocity of the gas, 1.1 m/sec .

31. A 25-ml volume of a solution containing a mixture of Pb^{II} and Bi^{III} salts is titrated with a 0.01*M* solution of complexon III at $\lambda = 240 \text{ nm}$. The complexonate of Bi^{III} is more stable than that of Pb^{II} and therefore two inflection points appear on the titration curve ($\epsilon_{\text{Pb} \cdot \text{EDTA}} > \epsilon_{\text{Bi} \cdot \text{EDTA}}$).

Calculate the contents of Pb and Bi if the values of optical density D_1 and D_2 before the point of equivalence, corres-

ponding to the volumes of added titrant, $V_1 = 1$ ml and $V_2 = 1.8$ ml, are known to be equal to 0.15 and 0.25, respectively. The optical densities of the solution, D' and D'' , after the first point of equivalence, corresponding to the volumes of titrant $V_1 = 3.0$ and $V_2 = 3.5$ ml, are equal to 0.75 and 1.00, respectively. The constant value of the optical density D_0 reached at the end of titration is 1.20. Disregard the dilution upon titration.

32. Figure 10 shows the absorption curves of complexes of metals with formaldoxime for solutions with an ion

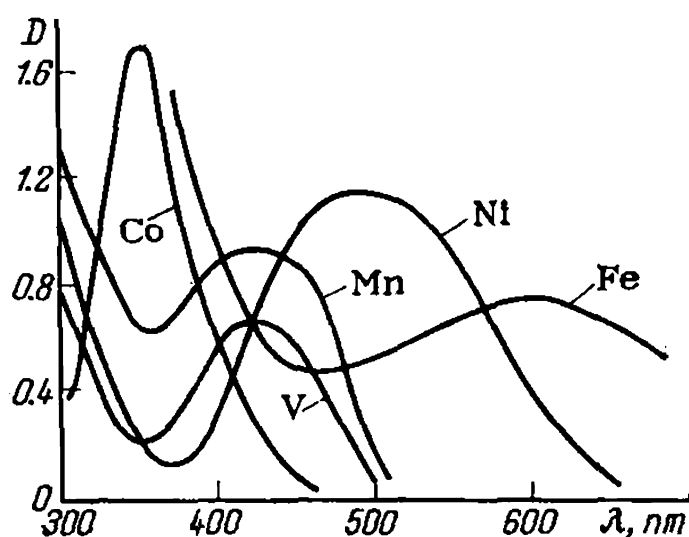


Figure 10

concentration of $4 \mu\text{g-ion/ml}$, obtained at a layer thickness of 1 cm in the cuvette.

What combinations of metal ions involving 2 and 3 ions can be determined as complexes with formaldoxime? Derive equations for determining the concentrations of cobalt and manganese in the mixture. Calculate the molar absorptivity for the maxima of the absorption spectrum curves shown in Fig. 10.

33. To plot a calibration graph in the spectrophotometric determination of hydrocyanic acid in air a standard solution of potassium cyanide was prepared. The titration of 25 ml of this solution required 23.85 ml of silver nitrate with a titre of 0.0350 mg/ml. This solution was diluted hundred-fold and the solutions indicated below were prepared from it. After these solutions reacted with bromine water and pyridine their optical densities were measured:

| | | | | | | |
|--|------|------|------|------|------|------|
| Volume of standard solution, ml | 0.25 | 0.50 | 0.75 | 1.0 | 1.5 | 2.0 |
| Volume of bromine water plus pyridine, ml | 4.75 | 4.50 | 4.25 | 4.0 | 3.5 | 3.0 |
| Optical density | 0.18 | 0.35 | 0.56 | 0.73 | 1.10 | 1.50 |

The passage of air through the absorbent and appropriate treatment resulted in 25 ml of a coloured solution with an optical density of 0.42.

Determine the concentration of HCN in the air (in mg/m^3) and figure out how much it exceeds the permissible limit ($0.3 \text{ mg}/\text{m}^3$).

34. Calculate the contents of copper, cobalt and nickel in a mixture from the light absorption by their diethyldithiocarbamate complexes (DDC) in chloroform at 436, 367 and 328 nm. The optical densities of the chloroform solution of the mixture of the ions to be determined as measured in a cuvette with a layer thickness of 1 cm were as follows:

$D_{436} = 0.45$; $D_{367} = 0.36$; and

$D_{328} = 0.86$. The volume of the solution analysed photometrically is 25 ml; the molar extinction coefficients (molar absorptivities) of the complexes in chloroform are:

| | | | |
|---|--------|--------|--------|
| λ , nm | 436 | 367 | 328 |
| $\epsilon_{\text{Cu(DDC)}_2}$ | 12,850 | 1260 | 2230 |
| $\epsilon_{\text{Co(DDC)}_2}$ | 2260 | 13,340 | 21,820 |
| $\epsilon_{\text{Ni(DDC)}_2}$ | 1,720 | 3,910 | 35,210 |

35. Figure 11 shows the spectrophotometric absorption curves for benzoyloxime at different values of pH: at pH = 2 the reagent is in the acidic form; at pH = 8.4 the acidic and salt forms coexist, and at pH = 11 the reagent is only in the salt form.

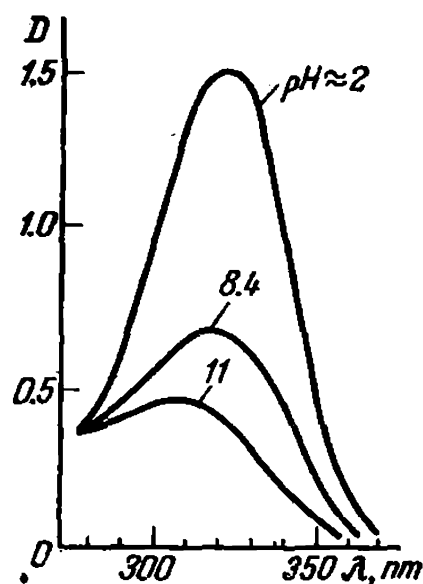


Figure 11

From the data given calculate the dissociation constant of benzoyloxime as a monobasic acid.

36. Determine the dissociation constant of a photometric reagent HR if at pH = 6.35 its optical density is 0.360 and at pH = 3.0 and 11.8 its optical densities are, respectively, equal to 0.890 and 0.025.

37**. Determine the composition of a complex of cobalt with nitroso-R-salt from the following results of a spectrophotometric determination obtained at $\text{pH} = 4.12$ and a wavelength of 570 nm:

| | | | | | | |
|--|------|------|------|------|------|------|
| Volume of cobalt solution, ml | 24.0 | 15.0 | 12.0 | 10.0 | 7.5 | 6.0 |
| Volume of solution of nitroso-R-salt, ml | 6.0 | 15.0 | 18.0 | 20.0 | 22.5 | 24.0 |
| Optical density | 0.28 | 0.95 | 1.14 | 1.32 | 1.48 | 1.29 |

The concentrations of the cobalt and nitroso-R-salt solutions are the same and equal to 10^{-3} mole/litre. The volume of a buffer solution added to the unknown solutions is 20 ml.

38**. Calculate the composition of a coloured compound of Pb^{2+} and pyridylazoresorcinol (PAR) by the mole-ratio method, using the following data:

| | | | | | |
|--|------|------|------|------|------|
| Concentration of PAR ($C \times 10^5$), mole/litre | 0.85 | 1.70 | 2.50 | 3.40 | 4.30 |
| Optical density | 0.18 | 0.39 | 0.59 | 0.78 | 0.92 |

| | | | | | |
|--|------|------|------|-------|-------|
| Concentration of PAR ($C \times 10^5$), mole/litre | 5.20 | 6.40 | 8.60 | 10.70 | 12.80 |
| Optical density | 1.00 | 1.04 | 1.05 | 1.06 | 1.04 |

The constant concentration of lead ions in the solutions is 4.4×10^{-5} g-ion/litre.

39**. In an analysis of a mixture of xylene isomers the radiation of 134.4 nm is used (the calibration graph is presented in Fig. 12).

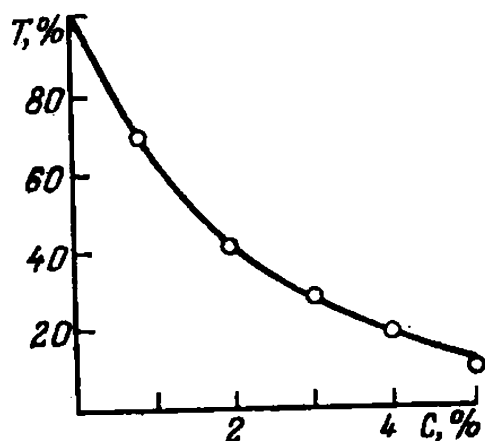


Figure 12

Which of xylene isomers can be determined in this analysis? Is the Bouguer-Lambert-Beer law obeyed?

Derive the equation relating the per cent absorption to the content of a xylene isomer and figure out the amount of the isomer corresponding to 0.75 per cent absorption.

40. For 10 per cent solutions of 2,5-, 2,3-dimethylhexane (2,5-DMH and 2,3-DMH) and 2,3,4-trimethylpentane (2,3,4-TMP) the following values for the absorption in the infrared spectral region were obtained:

| | | | | | |
|---------------------------------------|--------|-------|-------|--------|--------|
| Wave number, cm^{-1} | 8.00 | 9.62 | 10.86 | 13.02 | 13.31 |
| Absorption | | | | | |
| 2,5-DMH | 0.039 | 0.085 | 0.359 | -0.025 | -0.039 |
| 2,3-DMH | -0.016 | 0.024 | 0.017 | 0.013 | 0.201 |
| 2,3,4-TMP | -0.048 | 0.579 | 0.208 | -0.023 | 0.016 |

Choose the conditions for determination of these constituents and derive an equation for their determination. Find the composition of the mixture from the following data:

| | | | | | |
|-----------------------------------|-------|-------|-------|-------|-------|
| Wave number, cm^{-1} . . | 8.00 | 9.62 | 10.86 | 13.02 | 13.51 |
| Optical density | 0.024 | 0.310 | 0.420 | 0.05 | 0.150 |

41**. Figure 13 gives the infrared spectrum of phenylisocyanate.

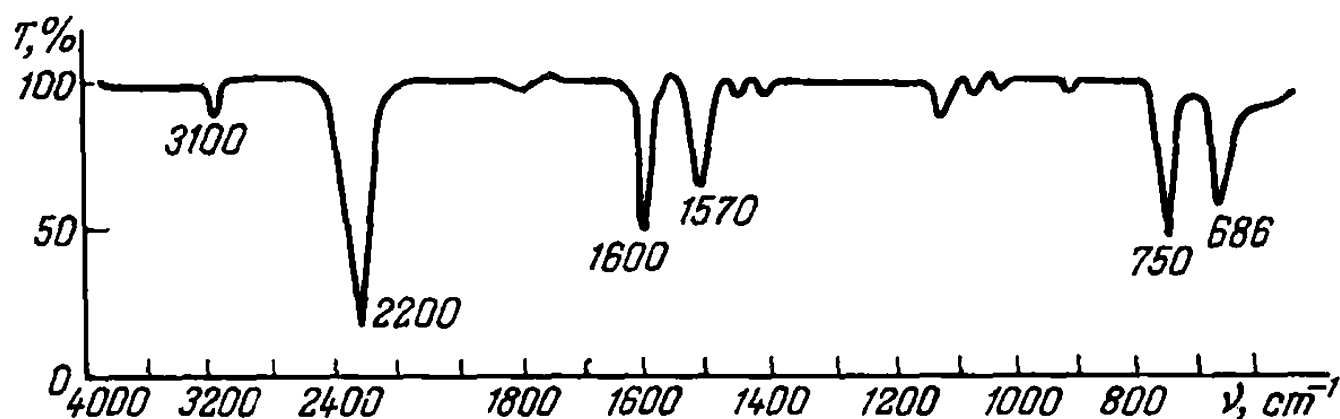
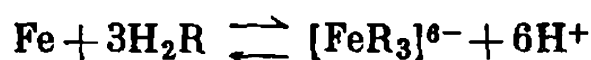


Figure 13

Find out to what functional groups vibrations with the wave numbers 3100, 2260, 1600, 1570, 750, and 686 cm^{-1} belong.

42*. Calculate the molar absorptivity and the stability constant of a sulphosalicylic complex of iron(III) formed by the reaction



The relation between the iron concentration and the optical density of the solutions measured at $\lambda = 430 \text{ nm}$ in a cuvette 2 cm in length is characterized by the following data:

| | | | | | | | |
|---|------|------|------|------|-------|-------|-------|
| $C_{\text{Fe}} \cdot 10^5$, mole/litre | 2.30 | 4.0 | 6.60 | 8.00 | 10.00 | 12.00 | 16.00 |
| D | 0.08 | 0.18 | 0.36 | 0.50 | 0.64 | 0.80 | 1.10 |

The dissociation constants of sulphosalicylic acid are $K_2 = 1.4 \times 10^{-3}$ and $K_3 = 1.8 \times 10^{-12}$; the pH of the solutions is 8.0.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. What are the advantages and shortcomings of spectrophotometric methods of analysis as compared with photometric?

(a) There appears no error due to the fading-out of the colour, but stricter observance of constant temperature is required.

(b) Mixtures of substances having different absorption maxima can be determined, but the monochromatization

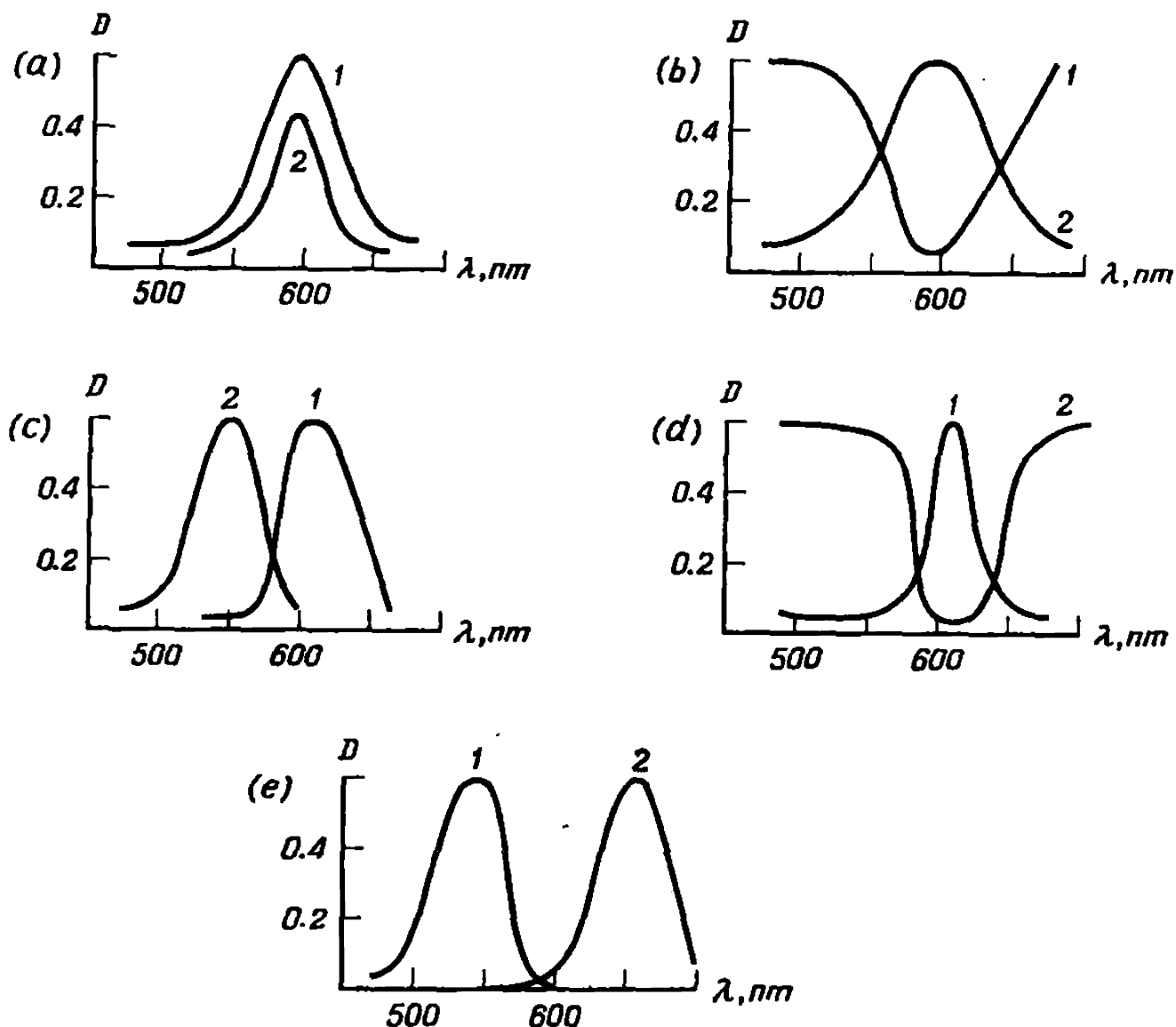


Figure 14

of light is required, which complicates the design of the apparatus used.

(c) No strict observance of the solution pH and of the colour maturation time is required, but spectrophotometric methods are less accurate.

(d) Conformity to the Bouguer-Lambert-Beer law is not required, but the light must be monochromated and the instruments employed are more sophisticated than those used for photometric analysis.

(e) No special advantages are offered by spectrophotometric methods.

2. What system of photocell "1" and light filter "2" must be chosen for investigating a solution which absorbs light in the 600 nm region (see Fig. 14)?

3. The optical density of a reagent is 0.03. After the addition of the unknown solution containing cadmium it increased to 0.58. When 2.0 μg of cadmium was added to the reagent under the same conditions, the optical density was found to be equal to 0.35. Which of the formulas given below should be used to calculate the content of cadmium in the solution if the Bouguer-Lambert-Beer law is followed over this concentration range?

(a) $\text{Cd} = 2.0 \times \frac{0.58}{0.35} = 3.38 \mu\text{g}.$

(b) $\text{Cd} = 2.0 \times \frac{0.35}{0.58} = 1.20 \mu\text{g}.$

(c) $\text{Cd} = 2.0 \times \frac{0.58 - 0.03}{0.35 - 0.03} = 3.45 \mu\text{g}.$

(d) $\text{Cd} = 2.0 \times \frac{0.58 + 0.03}{0.35 + 0.03} = 3.18 \mu\text{g}.$

(e) The data given are insufficient. The volume in which measurements are made must also be known.

4. The graphs given (see Fig. 15) show the properties of a coloured solution against a number of factors. Indicate the conditions suitable for the photometric determination of the given substance.

(a) At $\text{pH} = 8$ the coloration should be measured at a wavelength of 600-700 nm immediately after the colour is formed.

(b) The determination at $\text{pH} = 3$ is more sensitive and convenient. The colour should be measured immediately after its formation; the pH of the solution and the wavelength at which measurements are made must be strictly maintained.

(c) The determination at $\text{pH} = 3$ should be carried out in the region of wavelengths over 550 nm after the colour was matured for 12-20 minutes. Under these conditions the Bouguer-Lambert-Beer law is followed only up to concentrations not over $3 \mu\text{g/ml}$.

(d) The determination at $\text{pH} = 8$ must be made with the pH of the solution being strictly maintained after the solution has been exposed for 15 min at a wavelength above

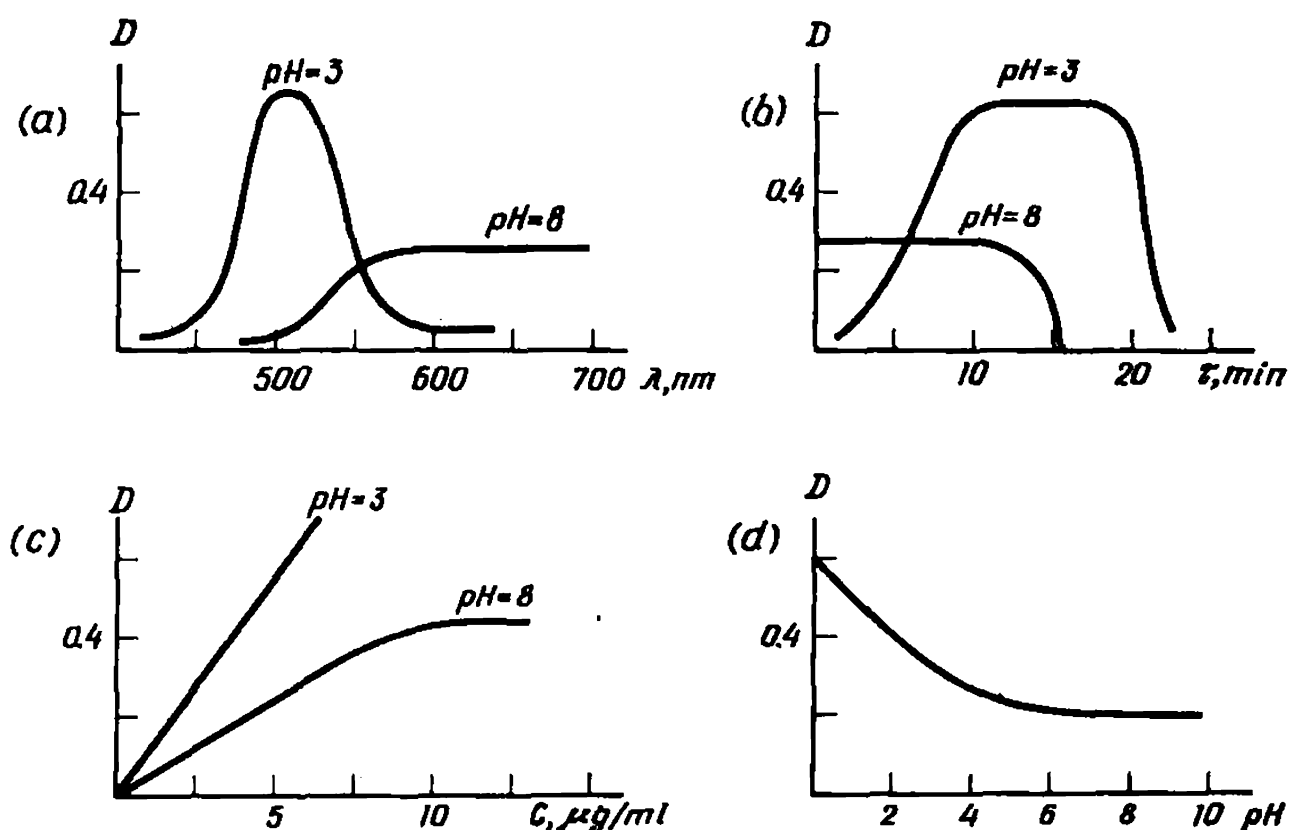


Figure 15

600 nm. The sensitivity of the determination under these conditions is very high.

(e) The determination can be carried out most conveniently at $\text{pH} = 8$ immediately after the formation of the colour. Strict observance of the pH and wavelength is not required, but the determination is less sensitive than at $\text{pH} = 3$.

(f) The determination at $\text{pH} = 8$ is inconvenient since it requires that the solution pH and the wavelength at which measurements are made be strictly maintained. The sensitivity of the determination in this case is the highest.

(g) Since the coloration at $\text{pH} = 3$ and 8 is strongly dependent on the time of maturation, the photometric methods are inconvenient for determination.

5. Indicate the conditions under which a photometric analysis must be conducted in the presence of a foreign coloured substance.

(a) A wavelength must be selected on the spectrophotometric curve at which the optical density of the coloured substance is minimal and the photometric analysis must be carried out at the chosen wavelength. In this case the foreign substance will not interfere with the determination.

(b) When comparing the spectrophotometric curves of the foreign and the unknown substance a wavelength is chosen at which the optical density of the foreign substance is lower than that of the unknown substance and the photometric analysis is carried out at the selected wavelength.

(c) The photometric analysis is carried out at different temperatures and at first the total optical density of the unknown and foreign substances is determined and then, at a different temperature, only the optical density of the foreign substance. The unknown substance is determined from the difference of the optical densities.

(d) If the concentration of the foreign substance is constant, it does not interfere with the photometric analysis. The calibration graph may pass above the zero in this case.

(e) Two photometric determinations are carried out, one at the maximum optical density of the substance being studied and the other at the maximum optical density of the foreign substance. The difference of these values is proportional to the concentration of the unknown substance.

(f) Two photometric determinations are carried out, one at the maximum optical density of the unknown substance and the other at the minimum optical density of the foreign substance. The difference of these values is proportional to the concentration of the unknown substance.

(g) If the maxima of the spectrophotometric curves of the unknown and foreign substances coincide and the concentration of the foreign substance is not constant, it must be removed by chemical means.

(h) If the foreign substance is coloured, it shall be removed.

(i) If the foreign substance is coloured, the photometric analysis must not be carried out.

6. Indicate in Fig. 16 the correct graph of photometric titration for the cases listed below. The symbols used are: X signifies the unknown substance, T is the titrant, and B is the reaction product.

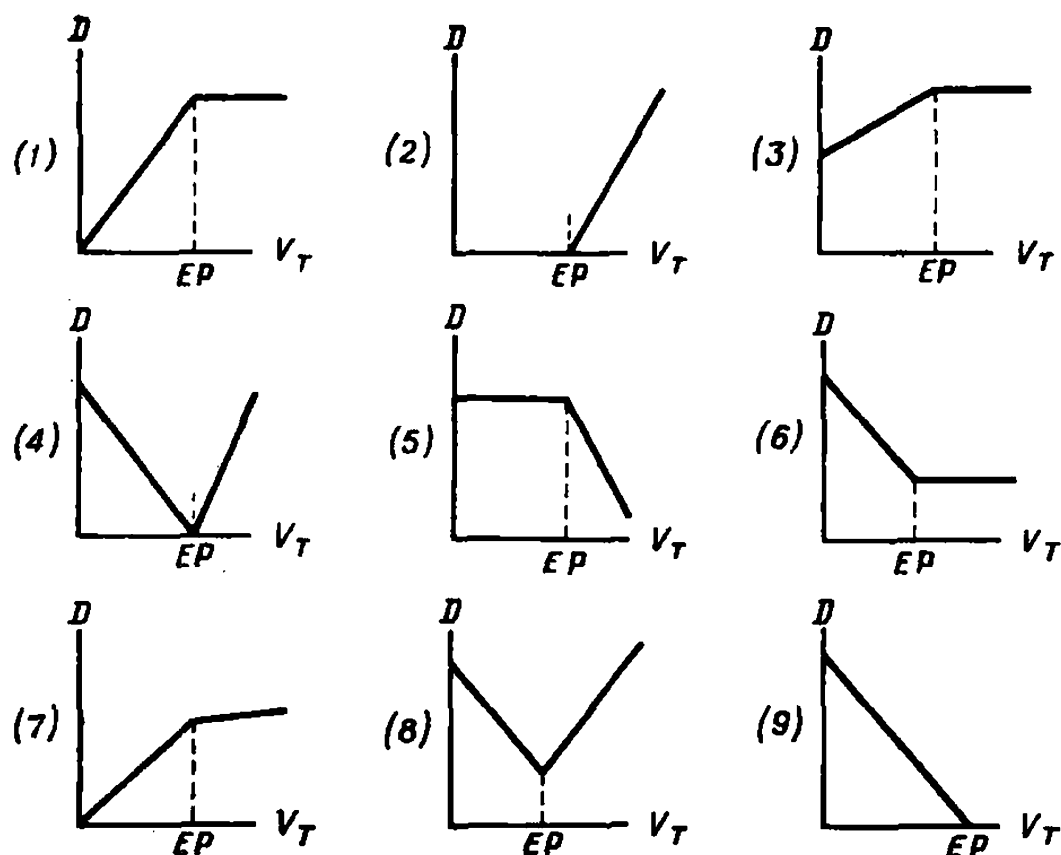


Figure 16

- (a) X and B are coloured and T is colourless.
- (b) T and B are coloured and X is colourless.
- (c) X and T are coloured and B is colourless.
- (d) T and B are colourless and X is coloured.
- (e) X and B are colourless and T is coloured.
- (f) T and X are colourless and B is coloured.

7. Find under B the formula for determination of the unknown concentration C_x by the method given under A, and under C indicate the specific features of the method chosen. The symbols used are: S signifies the readings on the diaphragm, D is the optical density, l is the layer thickness, and I is the intensity of the light beam.

A

(a) The method for determining the intensity of light beams.

(b) The comparison method.

(c) The standard addition method.

(d) The method of equalization of light beams by means of a diaphragm.

(e) The calibration graph method.

(f) The method of equalization of the thickness of the solution layer.

B

$$(1) C_x = C_{st} (\log S_x - \log S_{st}).$$

$$(2) C_x = \frac{\log I_x - \log I_0}{\varepsilon}.$$

$$(3) C_x = K D_x.$$

$$(4) C_x D_x = \text{const.}$$

$$(5) C_x = C_{st} \cdot \frac{D_x}{D_{st}}.$$

$$(6) C_x = C_{st} \cdot \frac{l_{st}}{l_x}.$$

$$(7) C_x = C_{st} (\log D_x - \log D_{st}).$$

$$(8) C_x = C_{st} \frac{D_{st}}{D_x}.$$

$$(9) C_x = \frac{\log I_0 - \log I_x}{\varepsilon l}.$$

$$(10) C_x = C_{st} \frac{l_{st}}{l_x}.$$

$$(11) C_x = \frac{D_x C_{st}}{(D_1 - D_x) \frac{V}{w} + D_1}.$$

C

(1) This method is used only in the ultraviolet region of the spectrum.

(2) No conformity to the Bouguer-Lambert-Beer law is required in this method.

(3) This method allows the measurements to be made over a comparatively narrow concentration range.

(4) This method requires the constancy of the initial light beam.

(5) This method is most often employed in photometry for mass analysis.

(6) This fast method is employed for individual analyses and it requires the adherence to the Bouguer-Lambert-Beer law.

(7) This method is used only in visual colorimetry.

(8) In this method, the reading scale of the instrument is logarithmic.

(9) This method is applicable only in the infrared region of the spectrum.

(10) No constancy of the initial light beam is required.

8. Figure 17 shows spectrophotometric curves for two

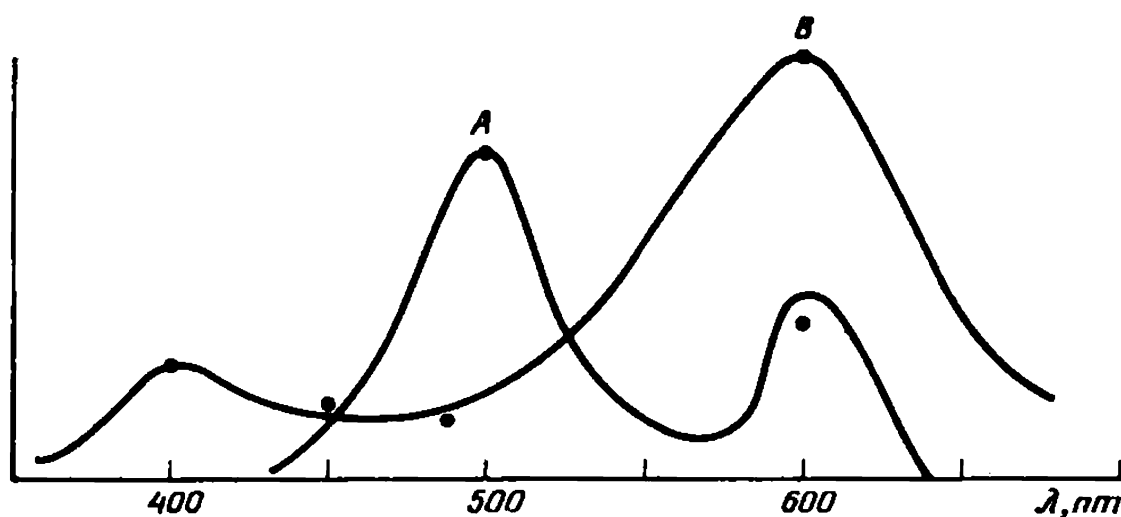


Figure 17

coloured substances. Indicate under A the correct answer as to the possibility of determining these substances separately, and under B the reason why the remaining answers are incorrect.

A

(a) Two substances, A and B, can be determined separately, A being measured photometrically at 500 nm and B at 600 nm.

(b) The substance A can be determined from the optical density at 500 nm, but it interferes with the determination of B.

(c) The substance B can be determined at a wavelength of 400 nm and when determining A a correction must be introduced for the optical density at 500 nm, corresponding to the optical density of B at this wavelength.

(d) The substance B can be determined at 400 nm and A at 600 nm, but when determining either of the substances a correction must be introduced for the content of the other.

(e) These substances cannot be separately determined photometrically.

B

(1) At 500 nm the optical density of B is rather high and may not be neglected. Under suitable conditions A does not interfere with the determination of B.

(2) The two components can be determined separately provided that suitable conditions are created.

(3) In the photometric determination of one component a correction must be introduced for the content of the other.

(4) At the specified wavelengths mutual interference is observed.

(5) When B is determined at 400 nm, a correction for the content of A need not be made. The optical density of A at 600 nm is low.

9. Indicate under B the conditions for the determination and in Fig. 18 the calibration graph which could be obtained for the cases of photometric determination listed under A.

A

(a) The determination of a substance in the presence of a coloured impurity of constant concentration if the comparison cell is filled with a solution containing the coloured impurity.

(b) The determination of a substance at a high concentration when the optical density is greater than 2.

(c) The determination of a substance in the presence of a colourless impurity capable of interacting with the reagent

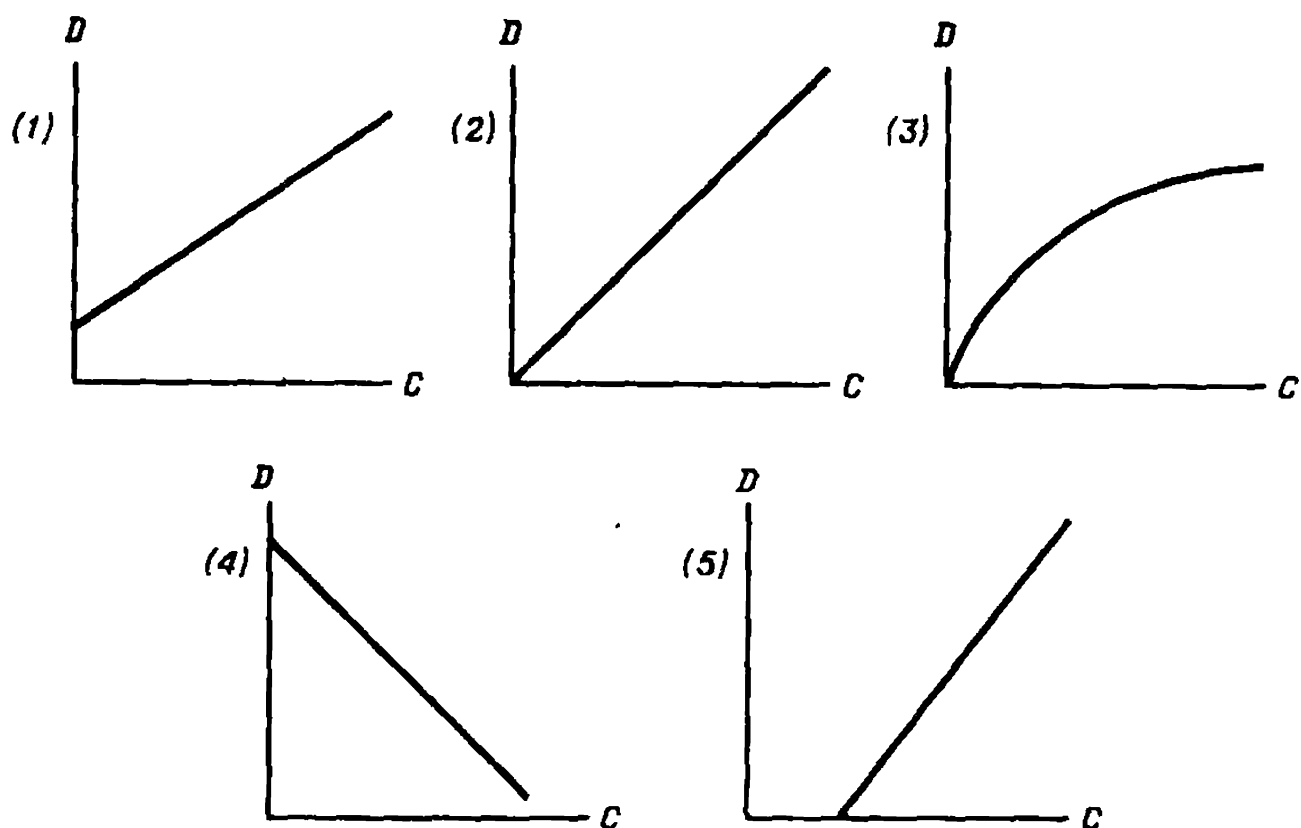


Figure 18

added. The comparison cell is filled with water. The absorption maxima for a compound of the reagent with the unknown substance and that with the impurity almost coincide.

(d) The determination of a substance in the presence of a coloured impurity capable of reacting with the added reagent to form a new colour. The absorption maxima for the impurity, its compound with the reagent, and the compound of the unknown substance with the reagent are quite different.

(e) The determination of a coloured impurity of varying concentration, which does not react with the reagent added.

B

(1) The comparison cell must be filled with the original coloured solution without addition of a reagent. The determination is possible if the colour of the impurity is not very intense.

(2) The determination is carried out with the comparison cell filled with a standard solution having a concentration close to the concentration of the substance being determined.

(3) The coloration of the impurity does not interfere with the determination in this case.

(4) The determination cannot be carried out in this case.

(5) The determination can be carried out if a suitable wavelength has been chosen from the absorption curves, at which the optical densities of the impurity and the compound formed by it are close to zero.

10. Indicate the correct circuit for photometric measurement by the Poggendorf compensation method (see Fig. 19)

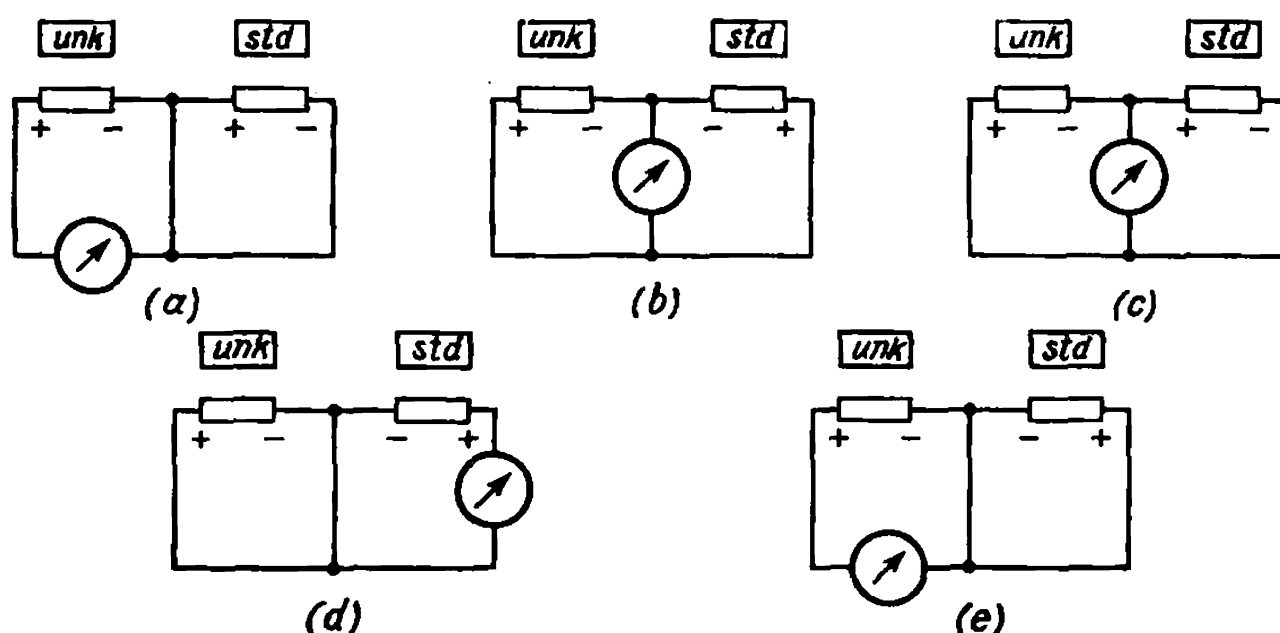


Figure 19

and the reason why the other circuits fail to yield the correct result:

(1) The readings of the galvanometer inserted into this circuit will not depend on the photocurrents.

(2) The galvanometer inserted into the circuit will not deflect at all.

(3) The galvanometer inserted into the circuit will show the photocurrent only from one photocell.

(4) The galvanometer inserted into the circuit will show the sum of the photocurrents from the first and second photocells.

(5) The galvanometer inserted into the circuit will show the difference of the photocurrents from the first and second photocells.

Refractometry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. Calculate the molar refraction for carbon tetrachloride if its refractive index is $n_D^{20} = 1.4603$ and its density $d_4^{20} = 1.604$. Compare the refraction found with that calculated from tables of atomic and bond (group) refractions.

Solution: We calculate the molar refraction from the formula

$$R = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$$

Substituting the values given, we have:

$$\begin{aligned} R &= \frac{154 (1.4603^2 - 1)}{1.6040 (1.4603^2 + 2)} = \frac{154 (2.1325 - 1)}{1.6040 (2.1325 + 2)} = \\ &= \frac{154 \times 1.1325}{1.6040 \times 4.1325} = \frac{174.23}{6.629} = 26.28 \end{aligned}$$

By reference to the tables of atomic refractions (see Lange's *Handbook of Chemistry*) we find refractions for carbon and chlorine to be $R_C = 2.418$ and $R_{Cl} = 5.967$.

Hence

$$R_{CCl_4} = R_C + 4R_{Cl} = 2.418 + 4 \times 5.967 = 26.29$$

From tables of bond refractions we find the refraction of the C—Cl bond, which is equal to 6.51, and calculate the refraction for carbon tetrachloride:

$$R_{CCl_4} = 4R_{C-Cl} = 4 \times 6.51 = 26.04$$

The agreement between the results is quite satisfactory.

Example 2. Calculate the refractive index of a substance and estimate the accuracy of the measurement if the limiting angle of deflection determined by a Pulfrich refractometer

equals $54^{\circ}25' \pm 2'$ and the refractive index of the prism glass is $N = 1.5147$.

Solution: We calculate the refractive indices for the limiting values of the angles (the upper limit is $\alpha_{\text{upper}} = 54^{\circ}23'$ and the lower limit, $\alpha_{\text{lower}} = 54^{\circ}27'$):

$$\begin{aligned} n_{\text{upper}} &= \sqrt{1.5147^2 - (\sin 54^{\circ}23')^2} = \sqrt{2.2943 - 0.6608} = \\ &= \sqrt{1.6335} = 1.2781 \end{aligned}$$

$$\begin{aligned} n_{\text{lower}} &= \sqrt{1.5147^2 - (\sin 54^{\circ}27')^2} = \sqrt{2.2943 - 0.6619} = \\ &= \sqrt{1.6324} = 1.2776 \\ n &= 1.2779 \pm 0.0002 \end{aligned}$$

Example 3. To determine the composition of water-acetone solutions the refractive indices of standard solutions were calculated:

| | | | | | |
|---------------------------------|--------|--------|--------|--------|--------|
| Percentage of acetone | 10 | 20 | 30 | 40 | 50 |
| Refractive index | 1.3340 | 1.3410 | 1.3485 | 1.3550 | 1.3610 |

Plot the calibration curve for determination of acetone, derive an equation relating the refractive index to concentration and determine, with the aid of the graph and the equation, the concentration of acetone in a solution whose refractive index is 1.3500.

Solution: We plot a graph of refractive index against concentration (see Fig. 20). The equation for the calibration graph is determined by the method of selected points. To do this, we select the following points at the ends of the straight line: $n = 1.3389$ for a concentration of 15 per cent and $n = 1.358$ for the 45 per cent concentration. We set up two equations

$$1.358 = A + B \times 45$$

$$1.3389 = A + B \times 15$$

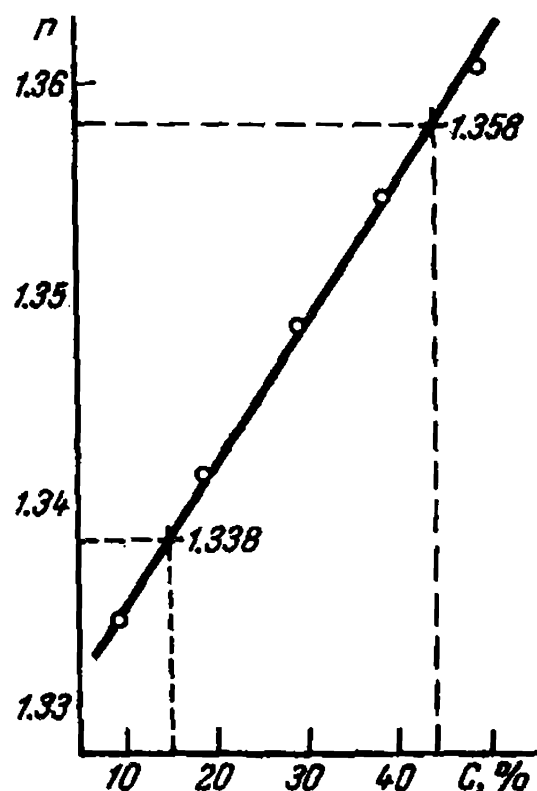


Figure 20

Solving these equations, we obtain: $A = 1.3279$ and $B = 6.7 \times 10^{-4}$.

Hence, the equation sought for has the following form:

$$n = 1.3279 + 6.7 \times 10^{-4} C$$

Using the calibration graph, we find that to the refractive index 1.3500 there corresponds a concentration of 33 per cent. Substitution of this value of the refractive index into our equation yields:

$$1.3500 = 1.3279 + 6.7 \times 10^{-4} C$$

Thus, we arrive at the concentration:

$$C = \frac{1.3500 - 1.3279}{6.7 \times 10^{-4}} = \frac{0.0221}{6.7} \times 10^4 = 33 \text{ per cent.}$$

2. MULTIVARIANT PROBLEMS

1*. Calculate the molar refraction for the substances listed in Table 14 from the data given in the table.

TABLE 14

| Variant | Substance | n_D^{20} | d_4^{20} |
|---------|---------------------------|------------|------------|
| I | Pentane | 1.3577 | 0.6262 |
| II | Methyl iodide | 1.5257 | 2.2790 |
| III | Bromobenzene | 1.5197 | 1.4950 |
| IV | Acetic acid | 1.3698 | 1.0493 |
| V | Pyridine | 1.5056 | 0.9831 |
| VI | Carbon sulphide | 1.6182 | 1.2631 |
| VII | Propyl alcohol | 1.3832 | 0.8035 |
| VIII | Nitrobenzene | 1.5455 | 1.2034 |

2. Table 15 gives the values of n_D^{20} , N and α found in measurements carried out with a Pulfrich refractometer. Find the parameter designated as x .

3. Assuming that there exists a linear relationship between the refractive index and the concentration (see Table 16), determine the concentrations of the unknown solutions from

TABLE 15

| Variant | Substance | n_D^{20} | N | α |
|---------|---|------------|--------|----------|
| I | Hexane | x | 1.6164 | 58°11' |
| II | Methyl alcohol | 1.3286 | 1.5335 | x |
| III | Bromobenzene | 1.5601 | x | 65°29' |
| IV | Toluene | 1.4969 | 1.7398 | x |
| V | Ethyl bromide | x | 1.7468 | 34.55° |
| VI | 30 per cent ethyl alcohol | 1.3535 | x | 53°10' |
| VII | Solution of H_3PO_4 (6 g/100 ml) | x | 1.6164 | 64°55' |
| VIII | Solution of NH_4Cl (15 g/100 ml) | 1.3606 | 1.6164 | x |

the concentrations of standard solutions and the refractive indices (or data for their determination). Assume that the densities of the standard and unknown solutions are equal.

3. PROBLEMS

SECTION A

1. To determine the composition of aqueous solutions of propyl alcohol the refractive indices of the standard solutions were found:

| | | | | | |
|------------------------------|--------|--------|--------|--------|--------|
| Percentage of propyl alcohol | 0 | 10 | 20 | 30 | 40 |
| Refractive index | 1.3333 | 1.3431 | 1.3523 | 1.3591 | 1.3652 |

Plot the calibration graph and determine the content of propyl alcohol in solutions, whose refractive indices are 1.3470 and 1.3615.

2. To plot a calibration graph in the refractometric determination of glycerine the following volumes of water and glycerine were measured out and the refractive indices of the mixtures obtained determined:

| | | | | | | |
|--------------------------------------|--------|--------|--------|--------|--------|--------|
| Volume of water, ml | 10 | 8 | 6 | 4 | 2 | 0 |
| Volume of glycerine, ml | 0 | 2 | 4 | 6 | 8 | 10 |
| Refractive index . . . | 1.3330 | 1.3627 | 1.3915 | 1.4211 | 1.4484 | 1.4740 |

TABLE 16

| Vari- ant | Solution | Concentration | | Refractive index n or data for its determination | | | Den- sity | Remarks |
|--------------|-----------------------------------|---------------------------------|-------------|---|--|-------------------------|--------------|---|
| | | C_{st} | C_x | solvent | standard solution | unknown solution | | |
| I | Ethyleneglycol in water . . | 50% | M g/ml | $n = 1.3330$ | $n = 1.3831$ | $n = 1.3546$ | 1.05 | |
| II | NaCl in water | 6% | | $n = 1.3330$ | $n = 1.3433$ | $n = 1.3382$ | 1.07 | |
| III | Benzene in CCl_4 | 40 mol. % | mol. % | $n = 1.4603$ | $n = 1.4767$ | $n = 1.4695$ | 1.33 | |
| IV | CCl_4 in aceto- ne | Pure CCl_4 | g/ml | $n = 1.3591$ | $n = 1.4603$ | $n = 1.4452$ | 1.20 | |
| V | Benzene in di- chloroethane | 50 mol. % | g/ml | $\alpha = 46^\circ 28'$ | $\alpha = 41^\circ 56'$ | $\alpha = 44^\circ 25'$ | 1.03 | $N = 1.6164$ |
| VI | Ethyl alcohol in water . . | 30% | g/litre | $\Delta = 16.9$ | $\Delta = 70.2$ | $\Delta = 45.6$ | 0.95 | Reading on scale of immersion refracto- meter |
| VII | Glycerine in water . . . | $C_1 = 20\%$ $C_2 = 50\%$ | M | — | $n_1 = 1.3575$ $n_2 = 1.3981$ | $n = 1.3785$ | 1.07 | |
| VIII | Acetone in wa- ter | $C_1 = 8.2\%$ $C_2 = 42.7\%$ | g/litre | — | $\alpha_1 = 36^\circ 08'$ $\alpha_2 = 33^\circ 28'$ | $\alpha = 35^\circ 25'$ | 0.96 | $N = 1.4704$ |

Plot a calibration graph for refractometric determination of the content of glycerine (in per cent by weight) in water if the density of glycerine is 1.26. Determine the content of glycerine in mixtures, whose refractive indices are 1.4050 and 1.4580.

3. To plot a calibration graph in the determination of the content of propyl alcohol in water the following data were obtained on the refractometer scale:

| | | | | | | | |
|---------------------------------|-----|-----|------|------|------|------|------|
| Percentage of alcohol | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Refractometer reading | 7.7 | 9.9 | 12.1 | 17.8 | 23.8 | 31.0 | 42.5 |

Plot a calibration graph and determine the content of propyl alcohol if the readings on the refractometer scale are 11.8 and 27.5 divisions.

4. The interferometric determination of the concentration of hydrochloric acid solutions yielded the following data:

| | | | | | |
|--------------------------------------|-------|-------|-------|-------|------|
| Concentration of acid, N | 0.205 | 0.400 | 0.605 | 0.805 | 1.05 |
| Compensator reading | 1.54 | 3.01 | 4.54 | 6.10 | 7.62 |

Plot the calibration graph and derive an equation expressing the dependence of the compensator scale readings on the concentration of hydrochloric acid. Determine the titre of a hydrochloric acid solution with respect to NaOH if the scale reading for the solution is 2.75.

5. Compute the refractive index of a substance if the limiting angle of deflection as determined with a Pulfrich refractometer is $52^{\circ}25'$ and the refractive index of the prism glass is $N = 1.62105$.

6*. Calculate the molar refraction of bromoform (tribromomethane) CHBr_3 if its refractive index is 1.5924 and its density, 1.5977. Compare the value obtained with the value calculated from the table of atomic refractions.

7. To determine the fat content in cocoa powder a sample weighing 1.500 g was treated with 2.50 ml of monobromonaphthalene, the refractive index of which is 1.6570. After the fat was extracted the refractive index of monobromonaphthalene dropped to 1.6420.

Find the fat content in the cocoa if the refractive index of pure cocoa fat is known to be 1.4630 and its density, 0.926.

8. In the interferometric determination of the content of hydrogen chloride in air the interferometer scale reading relative to pure air was 5.57 divisions. After 10 litres of the air was passed through water the titration of the absorbed hydrogen chloride required 10.5 ml of a 0.15*N* alkaline solution.

Determine the content of hydrogen chloride in 1 m³ of the air, for which the interferometer scale reading is 3.85 divisions, assuming that over this range of concentrations the interferometer scale reading is proportional to the content of hydrogen chloride.

SECTION B

9. The density of a liquid is 0.791, that of its vapours relative to air, 2.000, and the limiting angle of deflection measured with a Pulfrich refractometer having a prism, whose refractive index is 1.6170, equals 60°55'.

Compute the molar refraction of this compound.

10*. By reference to tables of atomic and bond refractions calculate the refraction of methylene iodide, CH₂I₂, and determine the refractive index of this compound if its density at 20 °C is 3.32.

11*. The refractive index of a 19.25 per cent solution of acetic acid is 1.3468.

Determine the normality of an acetic acid solution, whose refractive index equals 1.3385, assuming that there is a linear relation between the concentration of acetic acid and the refractive index over this range of concentrations.

12*. By using the data given in the handbook, plot a graph of the refractometer scale readings against the concentration of ethyl alcohol ranging from 0 to 20 per cent by volume, every other 5 scale divisions. To what concentration of the alcohol does the scale reading 31.5 divisions correspond?

13*. The hydrocarbon C₁₀H₁₆ has a refractive index of 1.4635 and a density of 0.8594.

Determine the molar refraction of this compound, suggest probable structures for it and find out which of these is most suitable for this compound according to the molar refractions of the bonds.

SECTION C

14*. By reference to tabulated data determine the molar refraction of ethyleneglycol and compare it with the value calculated from the structural formula of this compound.

15. To determine phenol in coal tar a portion of the tar weighing 2.25 g was treated with 5 ml of a 15 per cent alkaline solution and benzene to remove oil. The refractive index

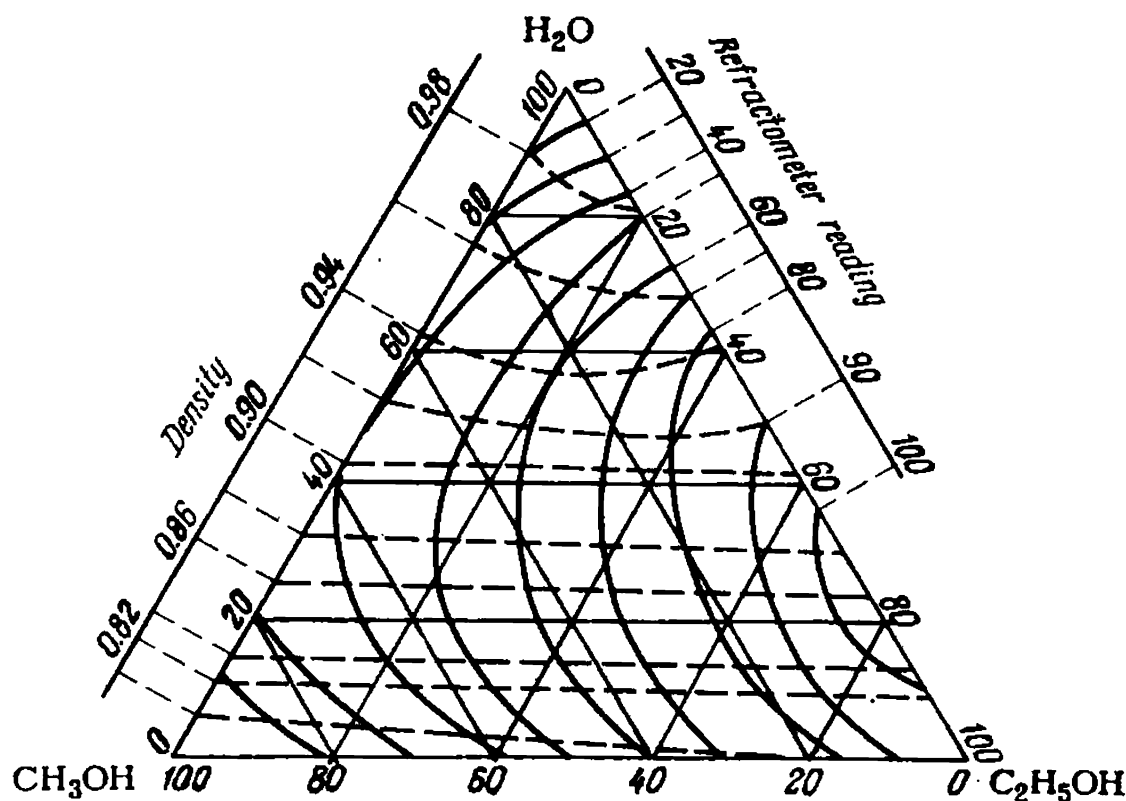


Figure 21. Diagram of a three-component system: methanol-ethanol-water. The solid line indicates the reading on the refractometer scale, and the dashed line, density.

of the alkaline solution is proportional to the amount of phenol extracted from the tar with alkali.

Determine the percentage content of phenol in the tar if the refractive index of pure phenol is 1.605, that of the 15 per cent alkaline solution, 1.373, and of the alkaline solution after extraction, 1.405. The density of phenol is 1.05.

16. Figure 21 is a diagram for a three-component system of water with methyl and ethyl alcohols.

By using this ternary diagram construct a series of diagrams for determining the concentrations of these alcohols from the densities and the scale readings of an immersion refractometer.

17**. The composition of an organic substance is: C = 60 per cent, H = 8 per cent, O = 32 per cent. The refractive index of this compound is 1.4045 and its density, 0.928.

Determine the nature of the carbon-oxygen bond ($=C=O$ or $\equiv C-O-C\equiv$) and the structural formula of this compound.

18. The refractive index of glycerine is 1.34550 before evaporation and 1.4145 after evaporation. Using the data in the handbook, determine the amount of water, in litres, evaporated from 10 litres of the initial solution, assuming that the amount of glycerine remains unchanged during the evaporation.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. Which of the following answers correctly characterizes the molar refraction?

(a) The molar refraction of a mixture is independent of temperature and is equal to the sum of the molar refractions of its constituents.

(b) The molar refraction is an additive property which means that it is independent of the composition of a mixture.

(c) The molar refraction of a mixture is little dependent on temperature and is equal to the sum of the molar refractions of its components with account taken of their molar fractions in the mixture.

(d) The molar refraction always increases as the concentration of the component in the mixture increases and falls with increase of temperature.

(e) The molar refraction is an additive property which means that it is equal to the sum of the molar refractions of the components in a mixture and is independent of temperature.

2. Which of the graphs shown in Fig. 22 reflects correctly the dependence of the molar refraction R on the density d at constant refractive index ($n_1 < n_2 < n_3$) and on the refractive index n at constant density ($d_1 < d_2 < d_3$)?

3. The refractive index of the prism glass in a Pulfrich refractometer is equal to 1.65 and the angle of maximum deflection for the liquid being studied is $23^\circ 48'$ ($\sin \alpha = 0.40$)

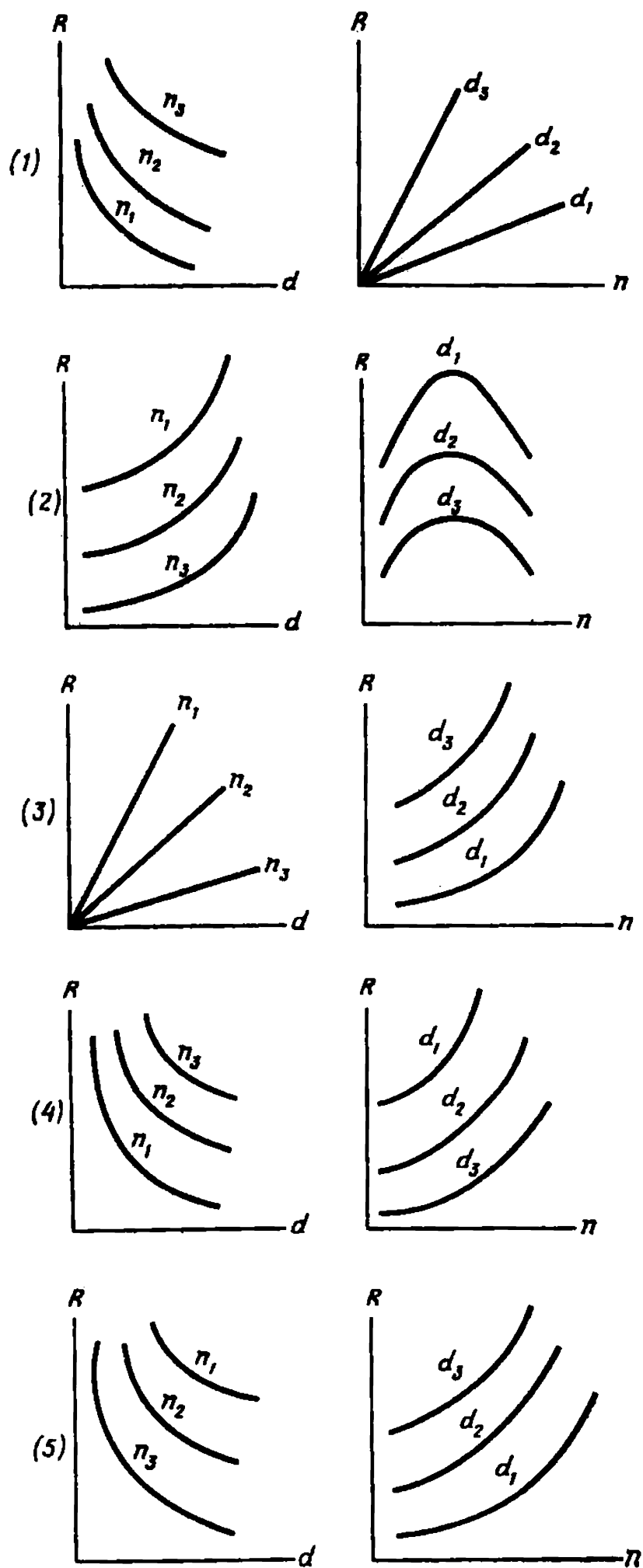


Figure 22

Which of the following formulas should be used to determine the refractive index of the liquid?

(a) $n = \sqrt{1.65^2 - 0.16} = 1.60.$

(b) $n = \sqrt{1.65 - 0.40} = 1.13.$

(c) $n = \sqrt{1.65^2 + 0.16} = 1.70.$

(d) $n = \sqrt{1.65^2 - 0.40} = 1.52.$

(e) $n = \sqrt{1.65^2 + 0.40} = 1.77.$

4. The reading on the scale of an immersion (dipping) refractometer is 65.2 for water and 78.5 for a 15-per cent alcoholic solution. Which of the following formulas should be used for calculating the percentage content of alcohol in the unknown solution if the reading on the refractometer scale is 73.3? There exists a linear relationship between the concentration and the refractometer scale readings.

(a) $C, \text{ per cent} = \frac{78.5 - 65.2}{15} \times \frac{73.5}{100} = 0.65.$

(b) $C, \text{ per cent} = \frac{78.5 - 65.2}{73.3 - 65.2} \times 15 = 24.7.$

(c) $C, \text{ per cent} = \frac{73.5 - 65.2}{78.5 - 73.3} \times 15 = 38.6.$

(d) $C, \text{ per cent} = \frac{73.3 - 65.2}{78.5 - 73.3} \times \frac{15}{100} = 0.386.$

(e) $C, \text{ per cent} = \frac{73.3 - 65.2}{78.5 - 65.2} \times 15 = 9.15.$

5. Which of the answers given below reflects correctly the dependence of the refractive index on various factors?

(a) The refractive index of some crystals varies with the direction of the light ray.

(b) With increasing temperature the refractive index of a gas falls and that of a liquid rises.

(c) The refractive indices of a liquid and its vapour are different, and their molar refractions are equal.

(d) The refractive index of a liquid does not depend on pressure and temperature.

(e) The refractive index of a mixture can be calculated by the additivity rule.

(f) With increasing temperature the refractive index of a gas always decreases.

(g) The refractive index of a liquid is directly proportional to the temperature.

(h) The dependence of the refractive index of a liquid on the light wavelength is expressed by a complex function.

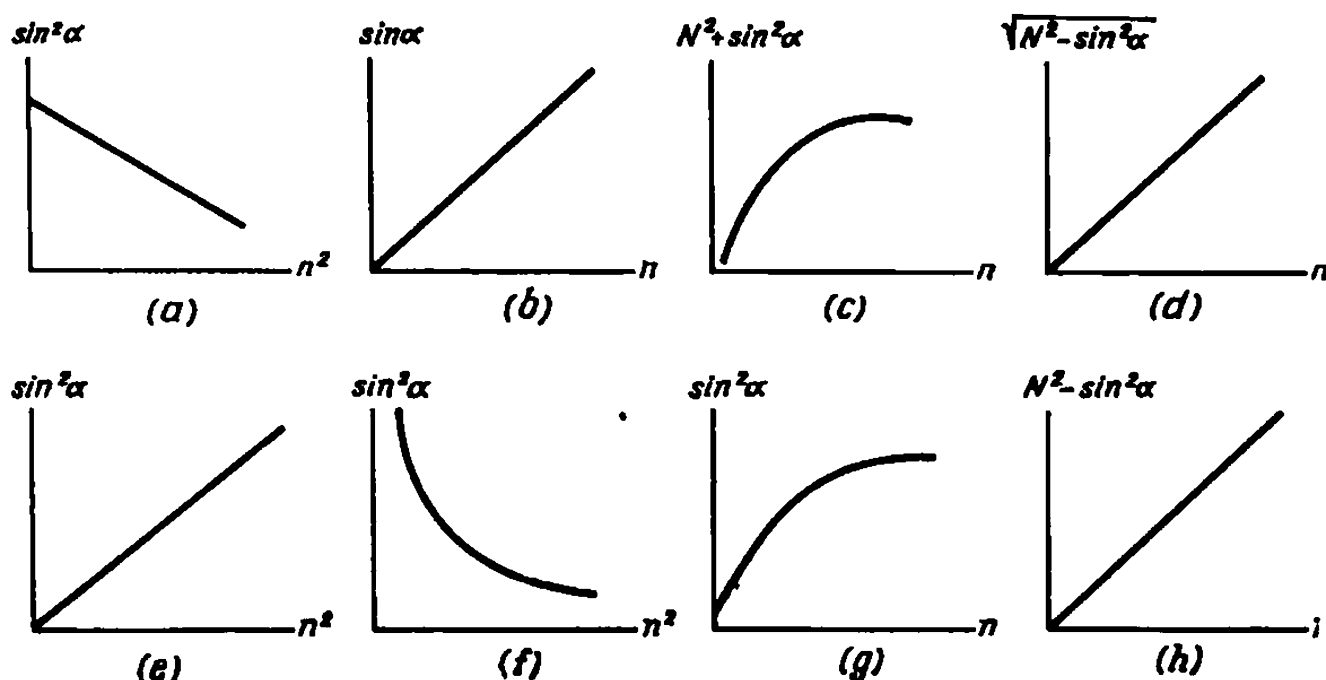


Figure 23

(i) Depending on the composition of a gas mixture its refractive index may either decrease or increase with rising temperature.

(j) With increasing temperature the refractive index of a gas always increases.

6. Which of the graphs (see Fig. 23) showing the dependence of the refractive index n on the angle of maximum deflection α obtained on a Pulfrich refractometer is correct?

7. Which of the following formulas should be used to calculate the molar refraction of acetic acid, CH_3COOH ?

(a) $R = R_{\text{H}} + R_{\text{C}} + R_{\text{O}}.$

(b) $R = 3R_{\equiv\text{CH}} + 2R_{=\text{CO}} + R_{-\text{OH}}.$

(c) $R = 4R_{\text{H}} + 2R_{\text{C}} + 2R_{\text{O}}.$

(d) $R = 4R_{\equiv\text{C}-\text{H}} + 2R_{=\text{C}=\text{O}} + R_{=\text{C}=\text{C}}.$

(f) This refractometer is inapplicable for investigating liquids whose refractive index is greater than $\sqrt{1.6^2 + 1}$.

(g) This refractometer is applicable for studying liquids whose refractive indices are within the following limits:

$$\sqrt{2.56} > n > \sqrt{1.56}$$

(h) This refractometer is applicable for analysing liquids whose refractive indices are within the following limits:

$$\sqrt{2.6} > n > \sqrt{1.6}$$

9. The concentration ternary diagram shown in Fig. 24 gives isolines for refractive indices from 1.4 to 1.55 and densities from 0.6 to 0.75. Find under B the answers to the questions put under A.

A

(a) What are the refractive index and density of a mixture of the following composition: 20 per cent A, 50 per cent B, and 30 per cent C?

(b) What are the refractive index and density of the pure component B?

(c) What is the composition of a mixture having $n = 1.45$ and $d = 0.70$?

(d) What are the refractive index and density of a mixture containing 60 per cent A and 40 per cent C?

(e) What are the refractive index and density of a mixture containing equal amounts of A, B and C?

(f) What is the composition of a mixture with $n = 1.50$ and $d = 0.70$?

(g) What are the refractive index and density of a mixture containing 50 per cent A, 25 per cent B, and 25 per cent C?

(h) What are the refractive index and density of a mixture containing 50 per cent B and 50 per cent C?

(i) What is the composition of a mixture whose density is 0.67 and refractive index, 1.44?

B

(1) A = 48 per cent, B = 17 per cent, C = 35 per cent.

(2) $d = 0.67$ and $n = 1.46$.

(3) $d = 0.70$ and $n = 1.46$.

(4) A = 23 per cent, B = 23 per cent, and C = 54 per cent.

(5) $d = 0.64$ and $n = 1.48$.

(6) $d = 0.62$ and $n = 1.47$.

(7) $d = 0.65$ and $n = 1.52$.

(8) $d = 0.72$ and $n = 1.44$.

(9) $d = 0.55$ and $n = 1.60$.

(10) This is impossible.

10. Under A indicate the factors that might be responsible for the appearance of a systematic error in the determination of the refractive index on a Pulfrich refractometer. Under B find the ways of eliminating the sources of error listed under A.

A

(a) The deviation of the acute angle of the prism from 45° .

(b) Incorrect graduation of the scale of the thermostat thermometer.

(c) The presence of an air layer between the prism and the cuvette.

(d) Incorrect graduation of the reading scale used for determination of the deflection angle.

(e) The difference between the glass used for the cuvette and that used for the prism.

(f) Absence of parallelism of the cuvette walls.

(g) The deviation of the straight angle of the prism from 90° .

(h) A systematic error appears if the refractive index of the liquid being determined is lower than that of the prism and cuvette glass.

(i) The deviation from the 1 : 2 ratio of the acute angles of the prism.

(j) The walls of the cuvette are not parallel to the plane of the prism.

B

(1) The systematic error introduced by this factor can be eliminated by introducing a correction factor.

(2) The systematic error introduced by this factor can be eliminated through calibration and calculation using correction tables and graphs.

(3) The systematic error introduced by this factor cannot be taken into account and the refractometer used is inapplicable.

(4) The systematic error introduced by this factor is very small and may be neglected.

(5) The indicated shortcoming does not lead to the appearance of a systematic error.

Polarimetry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. Determine the specific rotation of the plane of polarization for raffinose $C_{18}H_{32}O_{16} \cdot 5H_2O$ if the solution containing 5 g of raffinose in 1 litre rotates the polarization plane to the left by 1.3° , with the length of the tube being 25 cm.

Solution: Substituting the data given into the equation

$$\beta = \frac{\alpha l C}{1000}$$

yields

$$1.3 = \frac{\alpha \times 25 \times 5}{1000 \times 10}$$

$$\alpha = \frac{1.3 \times 1000 \times 10}{25 \times 5} = 104^\circ$$

Example 2. The specific rotation of the plane of polarization for nicotine $C_{10}H_{14}N_2$ equals 162° for the yellow sodium line.

Determine the concentration of a solution of nicotine (in moles/litre), which rotates the plane of polarization 0.52° to the left in a tube 10 cm in length.

Solution: Substituting the data given above into the equation

$$\beta = \frac{\alpha l C}{1000}$$

gives

$$0.52 = \frac{162 \times 10 \times C}{1000}$$

$$C = \frac{0.52 \times 1000}{162 \times 10} = 0.32 \text{ g/100 ml}$$

whence

$$M = \frac{0.32 \times 10}{162} = 0.020$$

where 162 is the mass of one mole of nicotine.

Example 3. In plotting the calibration graph for tartaric acid the following data were obtained on a wedge-type polarimeter:

| | | | | |
|--|-----|------|------|------|
| Concentration of solutions of tartaric acid, per cent | 10 | 20 | 30 | 40 |
| Polarimeter reading, mm | 9.9 | 19.1 | 27.3 | 34.9 |

How many grams of tartaric acid must be dissolved in 250 ml of water for the polarimeter scale reading to be 23.5 mm?

Solution: We plot the concentration of tartaric acid (in per cent) against the scale readings (see Fig. 25). From the graph we find that $C = 24.7$ per cent for 23.5 mm and calculate the weight of a sample of tartaric acid:

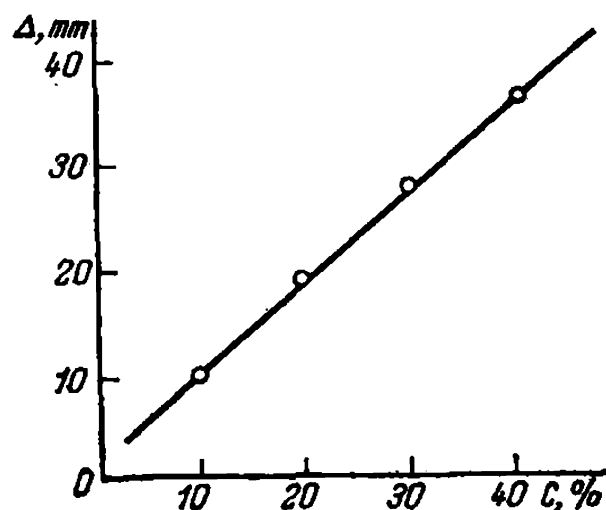


Figure 25

$$24.7 = \frac{g \times 100}{250 + g}$$

$$g = \frac{250 \times 24.7}{100 - 24.7} = 82.3 \text{ grams}$$

2. MULTIVARIANT PROBLEMS

Using the equation

$$\beta = \frac{\alpha l C}{1000}$$

determine the unknown parameter in Table 17.

TABLE 17

| Variant | Substance | α° | l , cm | C | β° |
|---------|--|----------------|----------|------------------|---------------|
| I | α -Asparaginic acid | -25.5 | 20 | x g/100 ml | -0.45 |
| II | Bromosuccinic acid | +41.9 | 10 | x mole/litre | +2.3 |
| III | Strychnine in alcohol | x | 25 | 0.45 g/100 ml | -1.17 |
| IV | <i>D</i> -Tartaric acid | +11.98 | 15 | 0.55 mole/litre | x |
| V | <i>L</i> -Borneol in alcohol | -37.7 | 25 | x g/100 ml | -1.25 |
| VI | Quinine | x | 20 | 0.017 mole/litre | -1.90 |
| VII | <i>L</i> -Alanine | +2 | x | 1.55 g/100 ml | 2.8 min |
| VIII | <i>D</i> -Inositol | +65 | 10 | 0.175 mole/litre | x min |

3. PROBLEMS

SECTION A

1. Determine the specific rotation of the plane of polarized light for *l*-morphine if the solution containing 0.45 g of *l*-morphine in 30 ml of methyl alcohol rotates the plane of polarization 4.92° to the left. The tube length is 25 cm.

2. The specific rotation of the polarization plane of grape sugar (glucose) is determined by the formula

$$\alpha_{20}^D = +52.5 + 1.88 + 10^{-2}C + 5.17 \times 10^{-3}C^2$$

where C is the concentration in grams per 100 ml.

Determine the angle of rotation of the polarization plane for a solution containing 3.4 g of glucose in 25 ml of water if the tube length is 20 cm.

3. The specific rotations of the polarization plane, α , for a 40 per cent solution of malic acid at 10, 20, and 30°C are $+1.31^\circ$, $+0.54^\circ$, and -0.12° , respectively.

Determine the angle of rotation of the polarization plane for a solution containing 5.55 g of malic acid in 50 ml at 25°C if the tube length is 15 cm.

4. The specific rotation of the polarization plane for glucose at various wavelengths has the following values:

| | | | | | |
|--------------------------------------|--------|--------|--------|--------|--------|
| Wavelength, nm . . . | 447 | 479 | 508 | 535 | 656 |
| Specific rotation, degrees | +96.62 | +83.88 | +73.61 | +65.35 | +41.89 |

Determine the specific rotation of the polarization plane for the characteristic hydrogen lines: yellow (589 nm), blue (486 nm), and violet (434 nm).

5. The specific rotation of the polarization plane for strychnine in an alcoholic solution at 20 °C is equal to -104° .

Determine the concentration of strychnine in the solution if the angle of rotation of the polarization plane is -1.56° in a 25-cm tube.

6. (+)-Malic acid rotates the plane of polarization to the right, and (—)-malic acid rotates it to the left. The specific rotation of the polarization plane for both acids is 2.3° .

Determine the content of (+)-malic acid in a solution for which the angle of rotation of the polarization plane is $+0.8^\circ$ if the total concentration of the acids is taken to be equal to unity.

7. In plotting the calibration graph for quinine the following data were obtained on a wedge polarimeter:

| | | | | | | |
|-------------------------------|-----|-----|-----|------|------|------|
| Percentage of quinine | 5 | 10 | 15 | 20 | 25 | 30 |
| Polarimeter reading, mm . . . | 2.7 | 5.5 | 8.4 | 11.4 | 14.3 | 17.7 |

Determine the quinine content if the scale readings are 10.3 and 15.8 mm.

8. For solutions containing 3.5 and 6.8 g of ascorbic acid in 25 ml of solution the readings obtained on the scale of a wedge polarimeter were 6.7 and 13.4 mm.

Determine the concentration of the ascorbic acid solution (in moles per litre) if the polarimeter scale reading is 10.3 mm.

SECTION B

9. A sample of saccharose weighing 0.859 ± 0.001 g was dissolved in water in a measuring flask with a capacity of 25.00 ± 0.01 ml. The angle of rotation of the polarization plane for the solution obtained is $2.28 \pm 0.02^\circ$ in a tube 10.00 ± 0.01 cm in length.

Determine the specific rotation of the polarization plane for saccharose, the accuracy of the determination and the source of the greatest errors.

10. The specific rotation of the polarization plane for a solution of strychnine in alcohol at a concentration of 2.25 g/100 ml is -139.3° and at a concentration of 0.254 g/100 ml it is equal to 104.3° .

Determine the concentration of the strychnine solution for which the angle of rotation of the polarization plane is 4.85° in a tube 25 cm in length.

11**. The specific rotation of the polarization plane for a crystal hydrate of Rochelle salt (potassium sodium tartrate), $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, is determined by the equation

$$\alpha_{20}^D = 27.14 + 9.92 \times 10^{-2}C - 9.4 \times 10^{-4}C^2$$

where C is the concentration of Rochelle salt in grams per 100 ml.

Determine the angle of rotation of the plane of polarized light for a solution containing 2.350 g of an anhydrous salt in 25.00 ml if the tube length is 15.00 cm. Determine the

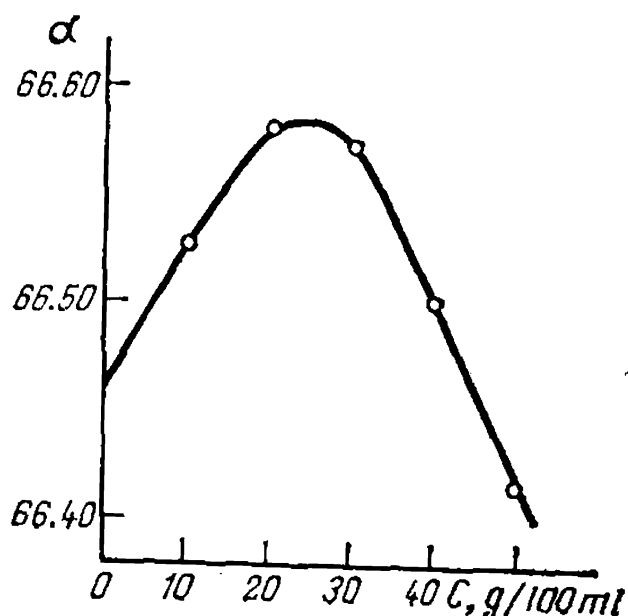


Figure 26

error which would be introduced into the calculation if the term containing C^2 or both terms containing C were dropped from the equation for specific rotation.

12. For D -mannose, $\text{C}_6\text{H}_{12}\text{O}_6$, at 20°C the specific rotation of the polarization plane for α -form is $+29.3^\circ$ and for β -form, -17.0° . A 3.68-g sample containing both forms was dissolved in 15 ml of solvent. This solution rotated the plane of polarized

light $+3.86^\circ$ in a tube 15 cm in length.

Determine the percentage content of α -form in the sample.

13. To extract brucine from a preparation, a sample weighing 25.00 g was treated with 200.0 ml of ethyl alcohol. The resulting solution rotated the plane of polarization 0.85° to the left in a tube 25 cm in length.

Determine the percentage content of brucine in the preparation if the specific rotation of the polarization plane for the alcohol solution of brucine is -80.1° . Calculate the accuracy of the determination if the angle of rotation of the polarization plane is read off with a precision of $\pm 0.02^\circ$.

14**. Determine the concentration of a solution of saccharose by referring to the plot of α against the saccharose concentration shown in Fig. 26 if in a tube 25 cm in length the angle of rotation of the polarization plane equals 61.53° .

SECTION C

15*. Determine the purity of *D*-tartaric acid (the specific rotation is $+12^\circ$) if a solution of this acid prepared by dissolving 2.57 g of the acid in 25.0 ml of water rotates the plane of polarized light 2.98° to the right in a tube 25 cm in length.

16*. A solution of 200 g of a natural substance containing *L*-scopolamine (the specific rotation is -28° in water and -18° in alcohol) and *L*-erythritol (the specific rotation is $+4.3^\circ$ in water and -11.1° in alcohol) in 200 ml of water rotates the plane of polarized light $+0.88^\circ$ in a tube 25 cm in length. A solution of 250 g of the same substance in 100 ml of alcohol rotates the polarization plane -3.61° , the tube length being the same.

Determine the percentage content of scopolamine and erythritol in the unknown sample.

17. The specific rotation of the polarization plane for ephedrine and pseudoephedrine in a 68 per cent water-ethanol solution at various wavelengths has the following values:

| | | | | | | | |
|----------------------------|------|------|------|------|------|------|-------|
| Wavelength, nm | 313 | 334 | 365 | 405 | 436 | 546 | 589 |
| Specific rotation, degrees | | | | | | | |
| ephedrine | 44.5 | 20.0 | 12.6 | 6.28 | 2.96 | 0 | -0.24 |
| pseudoephedrine | 108 | 173 | 138 | 107 | 86.7 | 54.2 | 46.1 |

Find the conditions for a polarimetric determination of ephedrine and pseudoephedrine in their mixture and set up the necessary equations for calculation.

18*. The hydrolysis of the saccharose of cane sugar resulted in the formation of α -*L*-glucose (the specific rotation is -95.5°) and α -*L*-fructose (the specific rotation is -152.6°)

in equivalent amounts. The original sugar solution rotated the polarization plane 5.75° to the right in a tube 25 cm in length. Some time after hydrochloric acid was added as a catalyst the angle of rotation of the polarization plane with the same tube became equal to 3.12° .

Find the amount of cane sugar (in per cent) that was hydrolysed.

19*. When saccharose (the specific rotation is $+66.5^\circ$) and *D*-glucose (the specific rotation is $+52.5^\circ$) react with potassium borohydride, the glucose is reduced and the saccharose remains intact. A solution containing glucose and saccharose rotated the polarization plane 4.3° in a tube 10 cm in length before the reaction with the borohydride and 2.9° after the reaction.

Find the contents of glucose and saccharose in the solution (in mg/ml).

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. On which of the factors listed below does the angle of rotation of the polarization plane depend?

- (a) The temperature and the nature of the solvent.
- (b) The nature of the solvent and of the solute.
- (c) The pressure, temperature and concentration of the solute.
- (d) The temperature, concentration and nature of the solute and the nature of the solvent.
- (e) The temperature and concentration of the solute.

2. For what purposes are additional Nicols or biquartz plates used in polarimeters?

- (a) They serve to increase the sensitivity of establishment of the optical equilibrium.
- (b) They serve to monochromate the light used for observation.
- (c) They are used to compensate the rotation of the plane of polarized light.
- (d) They are used to compensate the effect of the solvent on the rotation of the plane of polarized light.
- (e) They are used instead of an analyser.

3. What is a system of wedges used for in polarimeters?

- (a) They perform the function of an analyser.

(b) They are used to introduce a correction for a temperature change.

(c) They increase the accuracy of readings for the angle of rotation of the polarization plane.

(d) They enable mixtures of optically active substances to be determined on a polarimeter.

(e) They are used to compensate the rotation of the plane of polarized light.

4. Indicate the classes of substances, the concentration of which can be determined by means of polarimetry.

(a) Substances that react with the solvent to form stable complexes.

(b) Substances whose optical activity is associated with the specific features of their molecular structure.

(c) Substances that interact with the solvent to form optically active complexes.

(d) Substances whose optical activity is associated with the specificity of the crystal lattice structure of the substance being studied.

(e) The polarimetric method is applicable to any substances for determination of only small concentrations, of the order of 0.3 to 0.5 per cent.

5. The following data were obtained in studying a solution of a substance in an optically active solvent. For a solution containing 5 g/litre of the unknown substance the angle of rotation of the plane of polarized light was 5.2° , and for a solution containing 15 g/litre of the substance it was equal to 19.8° . Which of the formulas listed below should be used to calculate the concentration of the substance in the solution if the angle of rotation of the plane of polarized light for it is 10° ?

(a) $C = \frac{5}{5.2} = 9.6 \text{ g/litre.}$

(b) $C = \frac{15-5}{19.8-5.2} \times 10 = 7.0 \text{ g/litre.}$

(c) $C = 5 + \frac{10-5.2}{19.8-5.2} \times (15-5) = 8.3 \text{ g/litre.}$

(d) $C = 15 - \frac{10-5.2}{19.8-5.2} \times (15-5) = 11.7 \text{ g/litre.}$

(e) The data given are insufficient for determination of the concentration. The angle of rotation of the plane by the solvent must also be known.

6. Which of the following schemes of polarizers is correct? The designations are as follows: P = polarizer; B = bi-quartz; A = analyser; N = additional Nicol; C = cuvette; W = wedge compensator.

- (a) $P \rightarrow B \rightarrow C \rightarrow W \rightarrow A$.
- (b) $P \rightarrow A \rightarrow C \rightarrow W$.
- (c) $A \rightarrow N \rightarrow C \rightarrow B$.
- (d) $C \rightarrow P \rightarrow W \rightarrow A$.
- (e) $P \rightarrow A \rightarrow C \rightarrow W$.
- (f) $P \rightarrow C \rightarrow A$.
- (g) $P \rightarrow N \rightarrow C \rightarrow A$.
- (h) $P \rightarrow C \rightarrow W$.

7. How does the angle of rotation of the polarization plane depend on the concentration of an optically active substance in a solution?

(a) The angle of rotation increases with increasing concentration.

(b) With increasing concentration of a dextrorotatory substance the angle of rotation of the polarization plane increases.

(c) The absolute value of the angle of rotation of the polarization plane always increases with increasing concentration.

(d) The curve expressing the dependence of the angle of rotation of the polarization plane on the concentration passes through a minimum.

(e) Up to a certain limit the angle of rotation of the polarization plane is proportional to the concentration and beyond this limit it ceases to change with concentration.

(f) The relative value of the angle of rotation decreases with increase of the concentration of a levorotatory substance.

(g) The character of the relation between the angle of rotation of the polarization plane and the concentration depends on temperature and may be quite different.

(h) The angle of rotation of the polarization plane is directly proportional to the concentration of an optically active substance.

8. Figure 27 shows the curves expressing the dependence of the specific rotation of the polarization plane on wavelength

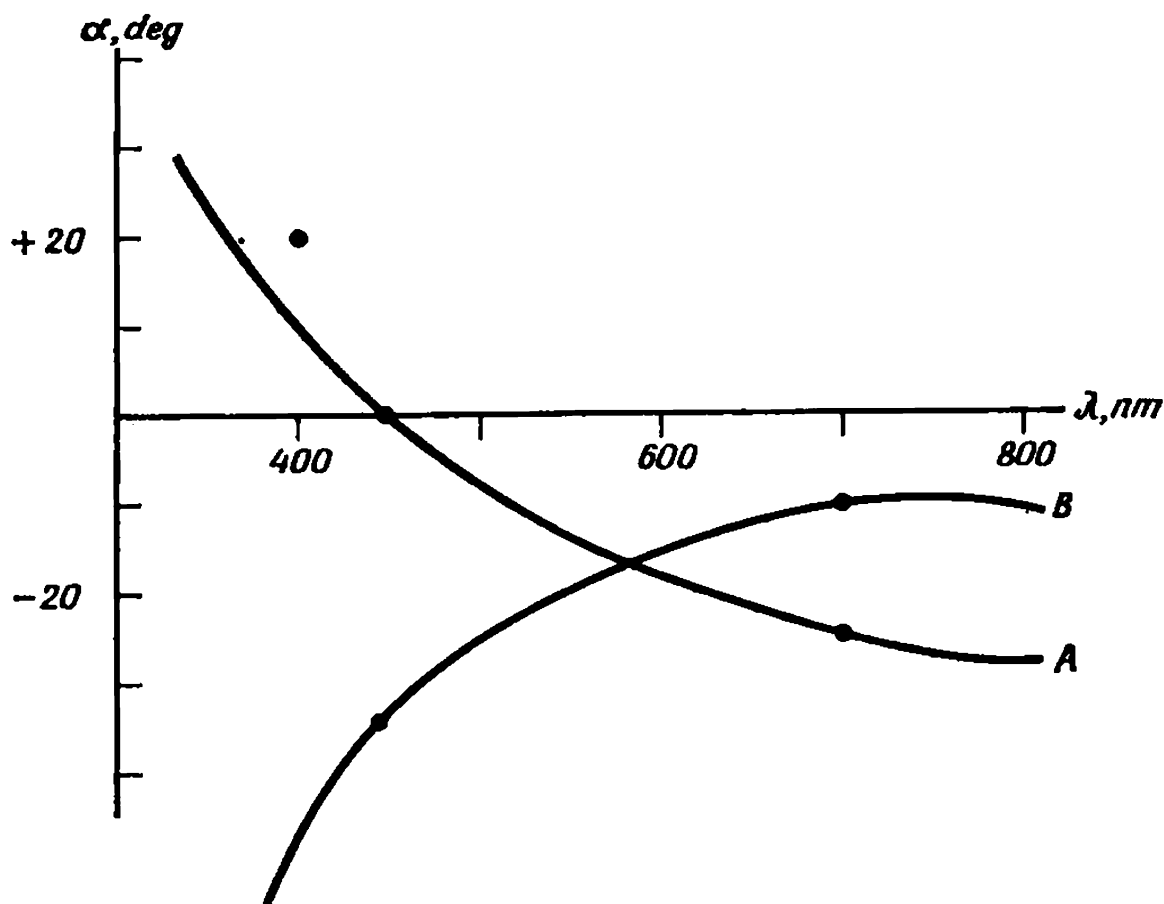


Figure 27

for two substances. Which of the formulas given below can be used to calculate the concentrations of these substances in the mixture if the length of the tube is 10 cm?

(a) $C_B = \frac{\beta_{450}}{(-30) \times 10}.$

(b) $C_A = C_B = \frac{\beta_{550}}{(-15) \times 10}.$

(c) $C_A = \frac{\beta_{700}}{(-25) \times 10}; C_B = \frac{\beta_{700}}{(-10) \times 10}.$

(d) $C_A = \frac{\beta_{700} - 1/3\beta_{450}}{(-25) \times 10}.$

(e) $C_A = \frac{\beta_{450}}{(-30) \times 10}.$

(f) The concentrations of A and B cannot be calculated from the data given.

9. How does the specific rotation of the polarization plane vary with increasing wavelength of monochromatic light?

(a) With increasing wavelength the absolute value of specific rotation increases.

(b) It is independent of the wavelength.

(c) The curve expressing the dependence of the specific rotation of the polarization plane on wavelength is complicated and passes through a series of minima and maxima.

(d) With increasing wavelength the specific rotation first increases and then remains constant.

(e) With increase of wavelength in the region of infrared waves the specific rotation of the polarization plane passes through a minimum.

(f) For a number of optically active substances the specific rotation changes its sign with increasing wavelength. The wavelength at which it is equal to zero is called the zero wavelength of the given substance.

(g) In the region of the visible light, the absolute value of specific rotation always decreases with increasing wavelength.

(h) It decreases with increase of the wavelength.

10. Find under B the ways of eliminating the shortcomings of a wedge-type polarimeter listed under A.

A

(a) The deviation of the cuvette length from that specified.

(b) The difference in the thicknesses of the movable and stationary wedges.

(c) Incorrect graduation of the scale of the movable wedge.

(d) The difference in the refractive indices of the cuvette and compensator wedges.

(e) The cuvette walls are not parallel.

(f) The difference in the absolute values of the angles of rotation of the stationary and movable wedges.

(g) Both wedges are made of dextrorotatory quartz.

(h) The presence of an air layer between the planes of the wedges.

(i) Incorrect calibration of the scale of the thermostat thermometer.

(j) The difference in the temperature between the unknown solution and the optical system of the polarimeter.

(k) Inaccurate observance of the wavelength of monochromatic light.

B

(1) This defect does not cause an error in the use of a polarimeter.

(2) This defect can be taken into account by introducing a correction factor.

(3) This defect can be taken into account through the use of correction tables or graphs.

(4) This defect cannot be eliminated and the polarimeter is inapplicable.

Other Optical Methods of Analysis

This chapter includes problems in the nephelometric, turbidimetric and luminescence methods of analysis. In distinction to the previous chapters, this chapter contains only two types of problems (A and B). Examples of problem-solving are omitted since the calculations in these analyses are analogous to those given in Chapters II and III.

1. PROBLEMS

SECTION A

1. To determine nephelometrically sulphate in brines a standard solution was prepared, which contained 7.5 g of anhydrous barium sulphate in 250 ml of water. After appropriate treatment aimed at producing suspensions of sodium sulphate the intensity of light scattered by a suspension of the standard was matched in a nephelometer with the intensity of light scattered by a suspension of the brine being analysed. The values obtained for the thickness of the liquid layers are: $l_{st} = 5.0$ cm, $l_x = 4.25$, 4.2, and 4.27 cm.

Determine the concentration of the sulphate in the unknown solution (in mg/ml) and the accuracy of the determination.

2. A 5-g sample of a salt was dissolved in 250 ml of water and when 5 ml of the solution was treated appropriately to produce a suspension of silver chloride it was diluted to 50 ml. The intensity of light scattered by the suspension was matched in a nephelometer with the intensity of light scattered by the standard. The standard solution was made

by dissolving 0.25 g of pure potassium chloride in 1.00 litre of water. After 7.50 ml of the standard solution was treated to produce a suspension of silver chloride it was diluted with water to 50 ml. The intensity of light scattered by the standard solution was found to be equal to 0.68 arbitrary unit and the corresponding value obtained for the unknown solution was 0.42 arbitrary unit.

Determine the percentage content of chlorine in the salt being analysed.

3. In a turbidimetric determination of lead as PbSO_4 use was made of a standard solution containing 0.25 g of $\text{Pb}(\text{NO}_3)_2$ in 100 ml of water. To plot the calibration curve different volumes of the solution were taken, which, after the addition of a stabilizing colloid and sulphuric acid, were made up to 50 ml with water. The optical densities of the solutions were then measured with a photoelectric colorimeter and the following data obtained:

| | | | | | |
|---------------------------------|------|------|------|------|------|
| Volume of standard solution, ml | 2 | 4 | 6 | 8 | 10 |
| Optical density | 0.15 | 0.25 | 0.32 | 0.39 | 0.45 |

A 50-ml volume of industrial water was diluted to 250 ml and 5 ml of the resulting solution was treated in the same way as the standard. The optical density of this solution was found to be equal to 0.35.

Determine the content of lead in industrial water (in g/m^3).

4. A sample of pyrite weighing 0.556 g was dissolved and the resulting solution was diluted with water to 250 ml; 5 ml of this solution after appropriate treatment gave 50 ml of a suspension of BaSO_4 , the optical density of which was found to be 0.45. For the calibration curve to be plotted the following data were obtained:

| | | | | | |
|--|------|------|------|------|------|
| Concentration of SO_3 , mg/ml | 0.05 | 0.10 | 0.16 | 0.22 | 0.27 |
| Optical density | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |

Determine the percentage content of sulphur in the pyrite.

5. A 0.75-g sample of a semiconducting metal was dissolved in 10 ml of solvent; when treated 1 ml of the solution gave 25 ml of a luminescent solution; the intensity of luminescence of the solution obtained was found to be equal to 35 arbitrary units.

Determine the content of selenium impurity in this metal by using the calibration graph given in Fig. 28.

6. The luminescence (fluorescence) intensity of an unknown solution of aluminium in 8-hydroxyquinoline was 0.99 arbitrary unit.

Determine the concentration of aluminium in this solution (in $\mu\text{g/ml}$) if the luminescence intensity of the standard solution containing 5 μg of aluminium in 1 ml was 0.45 arbitrary unit under the same conditions. The luminescence intensity under the conditions of the determination is proportional to the concentration of aluminium.

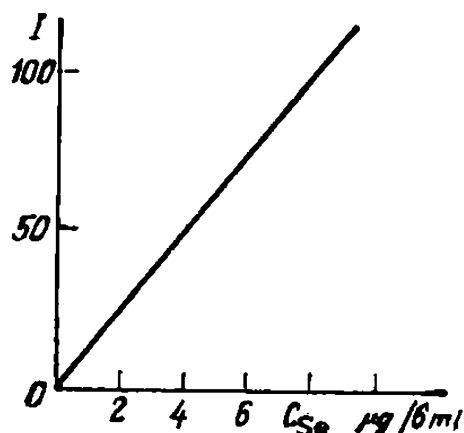


Figure 28

7. The luminescence intensity of a solution of 0.15 g of selenium was 0.25 arbitrary unit. After the addition of a standard solution containing 50 μg of gallium

the luminescence intensity increased to 0.75 arbitrary unit.

Determine the percentage content of gallium in selenium if the luminescence intensity of a blank solution is 0.05 arbitrary unit.

8. Different volumes of a standard solution containing 1 mg of copper in 1 ml were treated with a solution of luminogallion and diluted with water to 100 ml; the intensity of luminescence was then measured.

The results obtained were as follows:

| | | | | | |
|---|----|----|----|----|----|
| Volume of standard solution, ml | 2 | 4 | 6 | 8 | 10 |
| Luminescence intensity, arbitrary units | 22 | 37 | 51 | 65 | 79 |

A 1-g sample of a metal containing traces of copper was dissolved in acid and the solution was diluted with water to 10 ml. One millilitre of the solution was used to prepare 25 ml of a solution whose luminescence intensity was equal to 43 arbitrary units.

Determine the percentage content of copper in the metal.

9. The relation between the luminescence intensity of a solution of a mixture of luminol, copper ammoniate and hydrogen peroxide and the concentration of fluoroglucine used as inhibitor is characterized by the following data:

| | | | | | | | | |
|--|-----|-------|-------|-------|-------|-------|-------|-------|
| Concentration of fluoroglucine, $M \cdot 10^3$ | 0 | 0.013 | 0.023 | 0.071 | 0.141 | 0.269 | 0.446 | 0.708 |
| Luminescence intensity, arbitrary units . . | 180 | 143 | 90.4 | 53.3 | 38.5 | 27.3 | 20.2 | 14.3 |

Determine the concentration of fluoroglucine (in mg/ml) if its luminescence intensity is equal to 45 arbitrary units.

10. The calibration graph for luminescence determination of uranium in a solution of tributylphosphate is expressed by the equation

$$C = 2 \times 10^{-5} + 5 \times 10^{-4} \log I$$

where C is the concentration (g/ml) and I the luminescent intensity expressed in arbitrary units.

Determine the concentration of uranium (in g/ml) if its luminescent intensity is 50 arbitrary units.

11. To plot a calibration curve in the luminescent determination of zinc by the degree of quenching of the luminescence of rhodamine the following data were obtained:

| | | | | | | | |
|---|----|----|----|----|----|----|----|
| Concentration of zinc, $\mu\text{g}/5 \text{ ml}$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Luminescence intensity, per cent of the initial | 63 | 50 | 45 | 39 | 32 | 29 | 25 |

A 0.5-g sample of indium phosphide containing traces of zinc was treated appropriately to prepare 100 ml of a solution. The addition of 5 ml of this solution to rhodamine under the conditions in which the calibration curve was plotted reduced its luminescent intensity to 42 per cent.

Determine the percentage content of zinc in the sample.

SECTION B

12*. To plot a calibration curve in the determination of chlorine in nitric acid in a photonephelometer, type ФЭК-H-57, the following data were obtained:

| | | | | | |
|--|------|------|------|------|------|
| Concentration of Cl^- , mg-ion/ml . . | 0.05 | 0.10 | 0.14 | 0.19 | 0.24 |
| Optical density | 0.05 | 0.10 | 0.20 | 0.30 | 0.40 |

A 100-ml volume of nitric acid (density = 1.50 g/cm^3) was made up to 250 ml with water. To 25 ml of this solution were added silver nitrate and a stabilizing colloid, and the

volume was made up to 50 ml by adding water. The optical density of the resulting solution was 0.35.

Determine the chloride-ion content of the nitric acid (in per cent).

13**. To determine silver in indium 1 g of the metal was dissolved in acid and the resulting solution diluted to 50 ml. After appropriate treatment 10 ml of this solution gave 100 ml of a suspension of AgCl having an optical density of 0.45. After the addition of 10 ml of a standard solution containing 0.15 mg of Ag_2SO_4 in 100 ml, the optical density increased to 0.82.

Determine the content of silver (in atoms/cm³).

14. To determine iron in waste water by the luminescence intensity of its compound with stilbexone, a standard solution was prepared by dissolving 0.586 g of chemically pure Fe_2O_3 , containing 2.5 per cent of hygroscopic water, in 250 ml of water. Stilbexone was added to the following volumes of the standard solution, which were then made up to 100 ml. The following data were obtained:

| | | | | | | |
|---|------|------|------|------|------|------|
| Volume of standard solution, ml | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| Luminescence intensity, arbitrary units | 0.18 | 0.31 | 0.42 | 0.51 | 0.58 | 0.64 |

To 5 ml of the waste water being analysed there was added stilbexone and the solution obtained was diluted with water to 25 ml. The luminescent intensity of the resulting solution was found to be equal to 0.25 arbitrary unit.

Determine the content of iron in the waste water (in g/m³).

15. A 0.15-g sample of uranium ore was dissolved and after appropriate treatment the solution was diluted with water to 100 ml. The luminescence intensity of the solution was found to be equal to 60 arbitrary units. The addition of 5 μg of uranium to 20 ml of this solution raised the luminescence intensity to 110 arbitrary units. The luminescence intensity of a blank sample was equivalent to that of 1 μg of uranium.

Determine the content of uranium in the ore, in kilograms per ton, assuming that the luminescence intensity is proportional to the amount of uranium present.

16. To plot a calibration curve in the determination of chromium by the degree to which the luminescence (or

fluorescence) of triazinylstilbexone is quenched, the following data were obtained:

| | | | | | | | | |
|--|-----|-----|-----|-----|-----|-----|------|------|
| Concentration of Cr^{3+} ($C \cdot 10^7$), g-ion/litre . . . | 0.0 | 0.4 | 1.2 | 2.3 | 4.4 | 8.3 | 12.0 | 16.0 |
| Luminescence intensity, arbitrary units | 100 | 95 | 87 | 79 | 68 | 56 | 49 | 44 |

By using the method of least squares derive an equation for the calibration curve, assuming the following linear relation:

$$\frac{1}{I^2} - \frac{1}{I_0^2} = kC$$

where I is the luminescence intensity of the solution and I_0 the luminescence intensity of the blank sample.

Determine the concentration of Cr^{3+} (in g-ion/litre) from this equation if the luminescence intensity is equal to 75 arbitrary units.

17. Determine the concentration of β -naphthol (in mg/litre) by using the graph shown in Fig. 29 if it is known that the intensity of fluorescence under the given conditions reaches 0.6 in 650 seconds.

18**. A 5-litre volume of a gas containing varying amounts of NO_2 was bubbled through an absorbent, resorcinol was added to it and the luminescence intensity of the resulting solution determined. The nitric acid formed in the solution was titrated with a 0.1N KOH solution. The following data were obtained:

| | | | | | |
|---|-----|------|------|------|------|
| Volume of KOH solution, ml | 6.9 | 13.7 | 20.9 | 27.9 | 34.8 |
| Luminescence intensity, arbitrary units | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |

An average sample of the gas (5 litres) was passed every 10 minutes through the absorbent and the luminescence intensity of the solution obtained was measured:

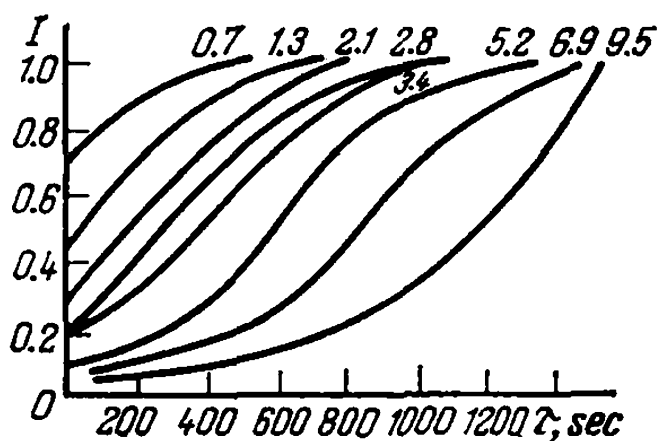


Figure 29. Variation of luminescence intensity with time versus the content of β -naphthol. The numbers on the curves signify the content of β -naphthol ($C \times 10^5 M$).

| | | | | | | | |
|---|------|------|------|------|------|------|------|
| Time, min | 0 | 10 | 20 | 30 | 40 | 50 | |
| Luminescence intensity, arbitrary units | 0.33 | 0.34 | 0.45 | 0.50 | 0.50 | 0.40 | |
| Time, min | 60 | 70 | 80 | 90 | 100 | 110 | 120 |
| Luminescence intensity, arbitrary units | 0.30 | 0.28 | 0.28 | 0.28 | 0.35 | 0.40 | 0.45 |

Determine the amount of NO_2 (in kg) that passed through a pipe if its cross-sectional area is 0.45 m^2 and the velocity of the gas stream, 1.1 m/sec .

2. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. Which of the requirements listed below must be satisfied in nephelometric and turbidimetric analyses and what impedes their realization?

(a) These analyses must be carried out at a strictly definite temperature and thermostating accurate to hundredths of a degree is very difficult to provide.

(b) In using these methods one must take measures for the suspensions formed to be made stable; the preparation of stable suspensions with particles of constant size presents the main difficulty.

(c) Since the reflected intensity is very low in a nephelometric analysis, one has to make use of highly concentrated solutions, and the difficulty encountered here is the necessity of using highly sensitive photomultipliers to pick up weak light beams.

(d) In these methods, all measurements should be made after the suspensions have completely settled, and for this to be accomplished it is necessary that no foreign components be present at all, which is difficult to achieve.

(e) In using these methods it is necessary that the light should be carefully monochromated and the main difficulty here lies in producing a powerful beam of monochromatic light.

2. Why is luminescence analysis used only for determination of small concentrations?

(a) At high concentrations the luminescence intensity is very high and the determination is hampered.

(b) At high concentrations there is observed a shift of luminescence towards the infrared region where visual observation becomes impossible.

(c) At high concentrations the intensity of luminescence strongly depends on temperature, pressure, the presence of impurities and the results are therefore difficult to reproduce.

(d) At high concentrations the spectral luminescence curve is shifted into the ultraviolet region and visual observation becomes difficult.

(e) At high concentrations there occurs a concentration quenching of the luminescence and it becomes weak.

3. Which of the following answers characterize the properties of and the advantages of using luminescence indicators?

(a) The use of redox indicators is associated with the fact that at the moment an equilibrium is attained between the oxidized and reduced forms of the indicator at a certain redox potential there arises intensive luminescence.

(b) The advantage of acid-base luminescence indicators is that their colour changes at different pH values.

(c) The use of redox luminescence indicators is accounted for by the fact that what emits luminescence is only the oxidized form of indicator, which is produced under the influence of the oxidant after the unknown substance has been titrated.

(d) An advantage of luminescence indicators is that coloured and transparent solutions can be titrated in their presence by different methods.

(e) The advantage of any luminescence indicator is that only a very small amount of it is required for the equivalence point to be determined.

4. In the determination of indium with rhodamine by the luminescence method the intensity of luminescence of the unknown solution was 20 units on the instrument scale. After the addition of 2 ml of a standard solution containing 0.25 $\mu\text{g/ml}$ of indium to 25 ml of the unknown solution, the luminescence intensity increased to 35 units. Which of the formulas given below should be used to calculate the concentration of indium in the unknown solution if there exists a direct proportionality between the luminescence intensity and the concentration?

$$(a) C = 20 \times \frac{0.25}{35 - 20} = 0.32 \mu\text{g/ml}.$$

$$(b) \ C = \frac{0.25}{35 \left(\frac{25+2}{20} \right) - 20} = 0.012 \text{ } \mu\text{g/ml.}$$

$$(c) \ C = \frac{0.25 \times 2}{30 \left(\frac{25+2}{20} \right) - 25} = 0.023 \text{ } \mu\text{g/ml.}$$

$$(d) \ \bar{C} = \frac{0.25 \times 2}{35 - 20} \times 20 = 0.64 \text{ } \mu\text{g/ml.}$$

(e) The data given are insufficient for the concentration to be determined. Another portion of the standard solution must be added and the measurements repeated.

5. Which of the answers given characterizes correctly the dependence of the intensity of the light scattered by the solid suspended particles present in the solution on various factors?

(a) The intensity of scattered light is proportional to the difference in the refractive indices of the solvent and suspended particles.

(b) The scattered intensity is inversely proportional to the incident wavelength.

(c) The scattered intensity is the higher the greater is the number of particles in a unit volume and the larger is the volume of the particles themselves.

(d) The scattered intensity is independent of the frequency of the incident light.

(e) The scattered intensity is inversely proportional to the radius of a suspended particle.

(f) The intensity of scattered light is directly proportional to its frequency raised to the fourth power.

(g) The scattered intensity is directly proportional to the wavelength raised to the fourth power.

(h) The scattered intensity is independent of the size of the suspended particles but depends on their nature.

6. Which of the answers given characterizes correctly the phenomenon of luminescence quenching?

(a) Quenching in the presence of foreign substances is attributed to the fact that a foreign substance emits luminescence, the luminescence of the unknown substance becoming increasingly weak.

(b) The luminescence is quenched when the wavelength of the exciting light exceeds a certain value.

(c) The luminescence is always quenched as the pH of the solution increases.

(d) The quenching of luminescence by foreign substances (particularly by the oxygen of the air) is associated with

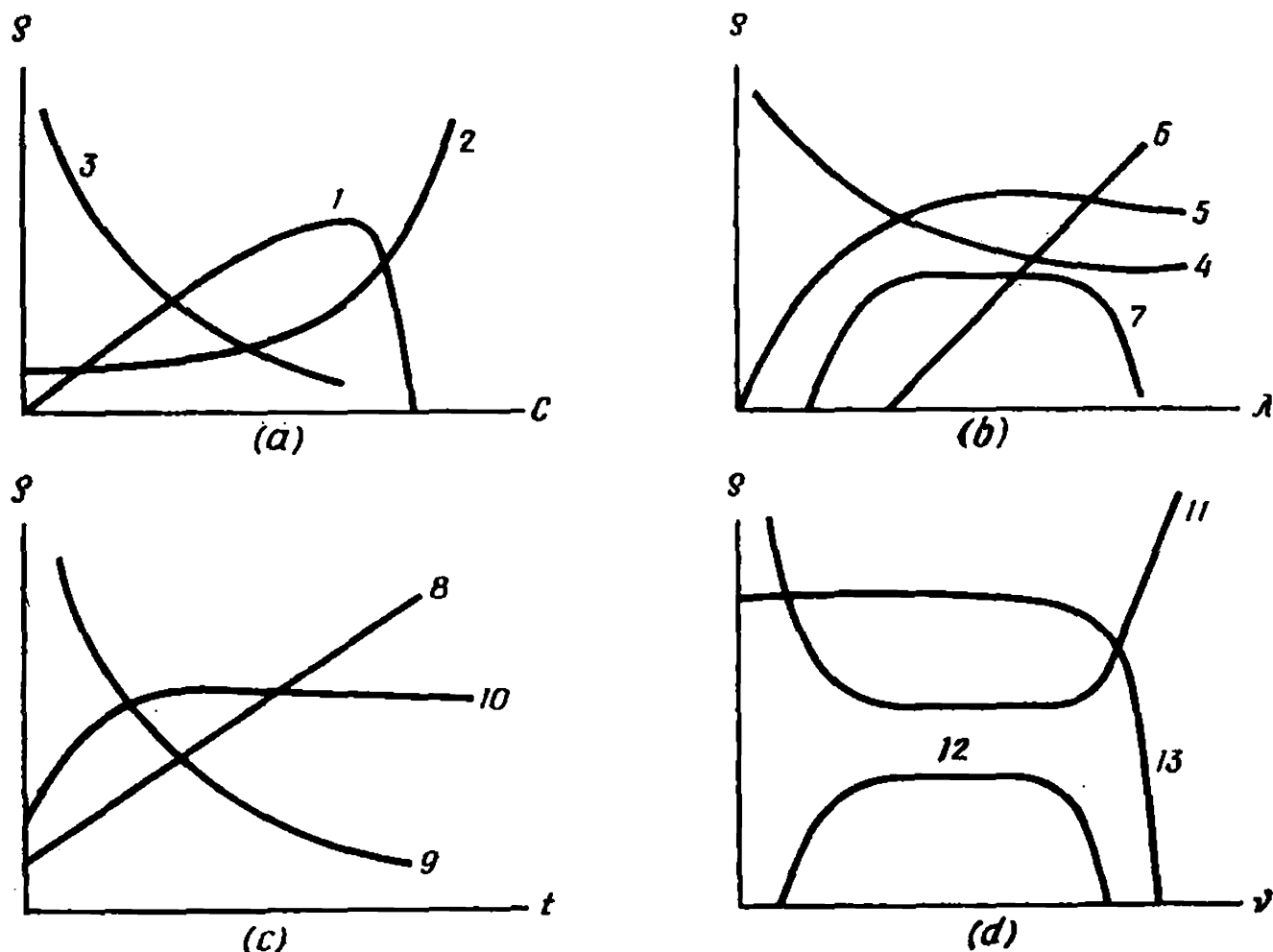


Figure 30

the interaction of these substances with a fluorescing substance, which results in the formation of nonfluorescing products.

(e) The luminescence is quenched when the temperature falls abruptly.

(f) The luminescence is quenched by foreign substances because they change the ionic strength of the solution.

(g) The presence of impurities results in the luminescence being quenched and therefore they must be removed from the solution.

(h) The luminescence is quenched as the concentration of the luminescent substance exceeds a certain value.

7. Which of the graphs shown in Fig. 30 reflects correctly the dependence of the luminescence yield on the concentration, temperature, and the wavelength and frequency of the exciting light?

8. Figure 31 is a diagram illustrating the excitation of luminescence. In Fig. 32 indicate the graph that shows correctly the spectrophotometric curves for the instruments shown in Fig. 31. (The numbers correspond to those in Fig. 32.) Indicate the reason why the other graphs cannot be used.

(a) In this case the light filter 4 will absorb luminescent radiation.

(b) In this case the light filter 4 will absorb luminescent radiation, the uviol filter 2 will transmit the rays emitted during luminescence, and the photocell 5 will be insensitive to the luminescent radiation.

(c) In this case the photocell 5 is insensitive to luminescent radiation.

(d) In this case the light source 1 emits an energy which will not excite luminescence, and the uviol filter 2 will pass the rays emitted during luminescence.

(e) This graph corresponds to the correct juxtaposition of the spectrophotometric curves of the instruments.

9. Indicate the conditions corresponding to the graphs of luminescence titration shown in Fig. 33. The designations used are: TS = substance being titrated; T = titrating solution; RP = reaction product.

(a) Such a graph results if TS emits a weak luminescence, T is non-luminescent, and RP is strongly luminescent.

(b) Such a graph will be obtained if TS and T do not emit luminescence, and RP is strongly luminescent.

(c) Such a graph will result if TS and T are strongly luminescent and RP is non-luminescent.

(d) Such a graph will result if T destroys luminescence and TS and RP are weakly luminescent.

(e) Such a graph will be obtained if T eliminates completely the luminescence of TS.

(f) Such a graph will result if TS and RP do not emit luminescence and T shows a strong luminescence.

(g) Such a graph will result if all the three substances, TS, T, and RP, emit a strong luminescence.

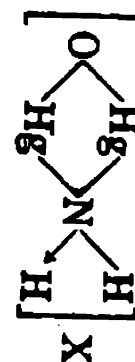
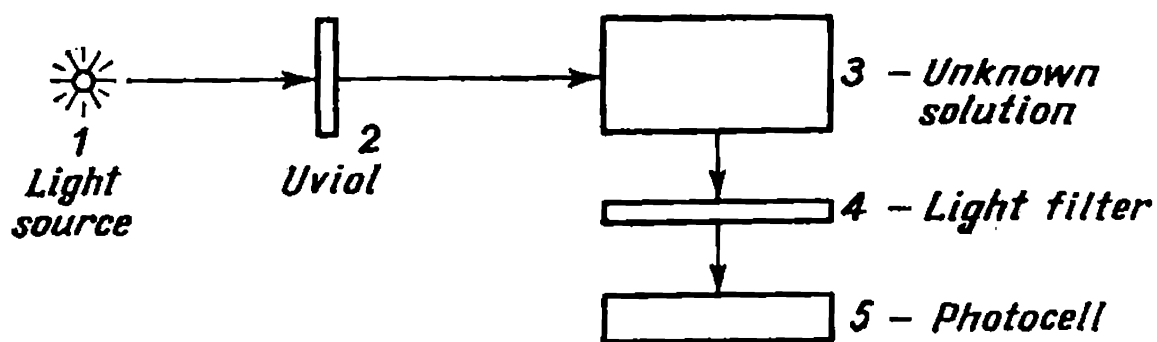


Figure 31

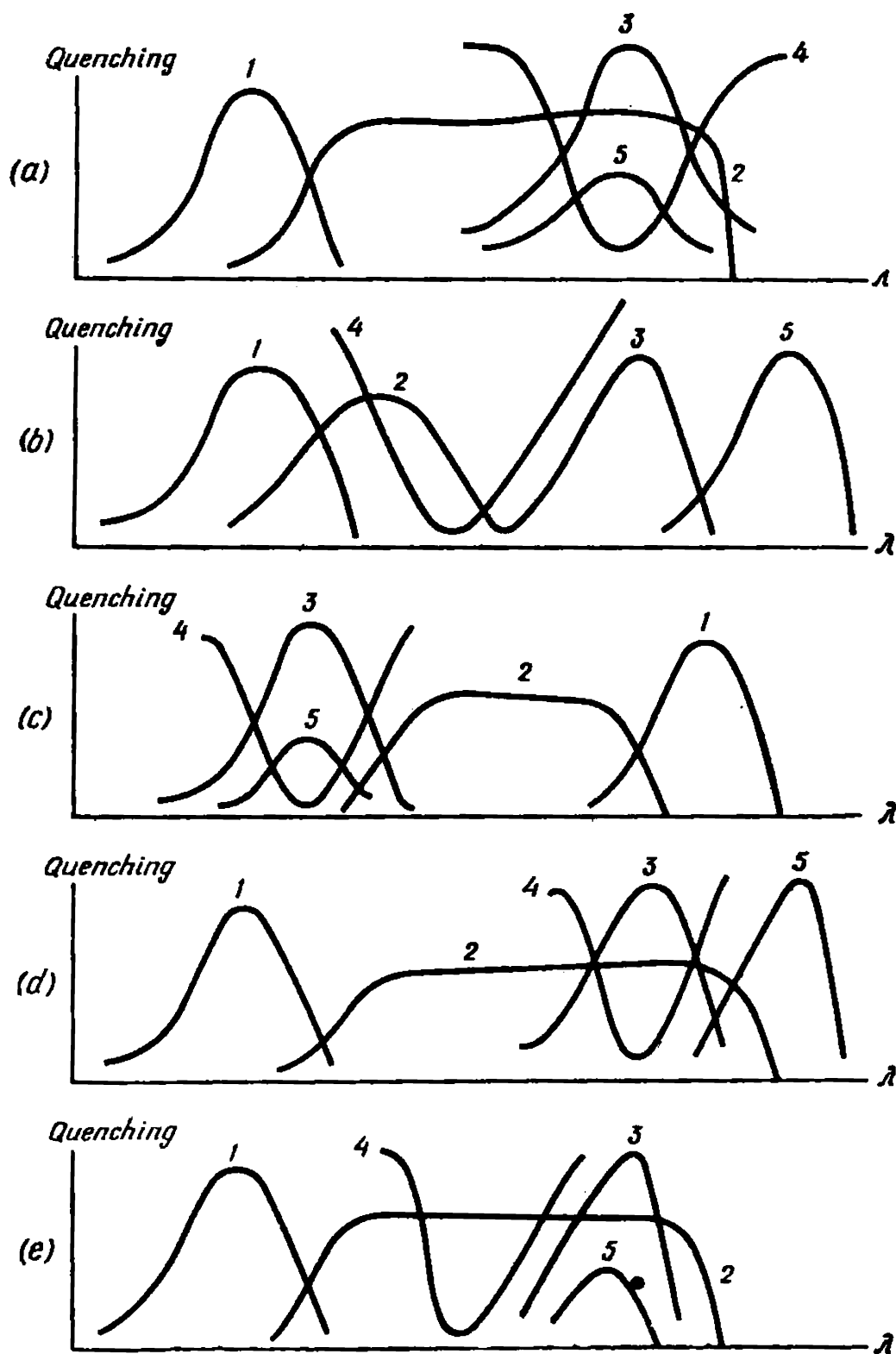


Figure 32

(h) Such a graph will obtain if TS, T and RP emit a weak luminescence.

(i) Such a graph cannot be obtained in luminescence titration.

10. Figure 34 shows schemes for transfer of electrons from various levels and sublevels of molecules. Which of the

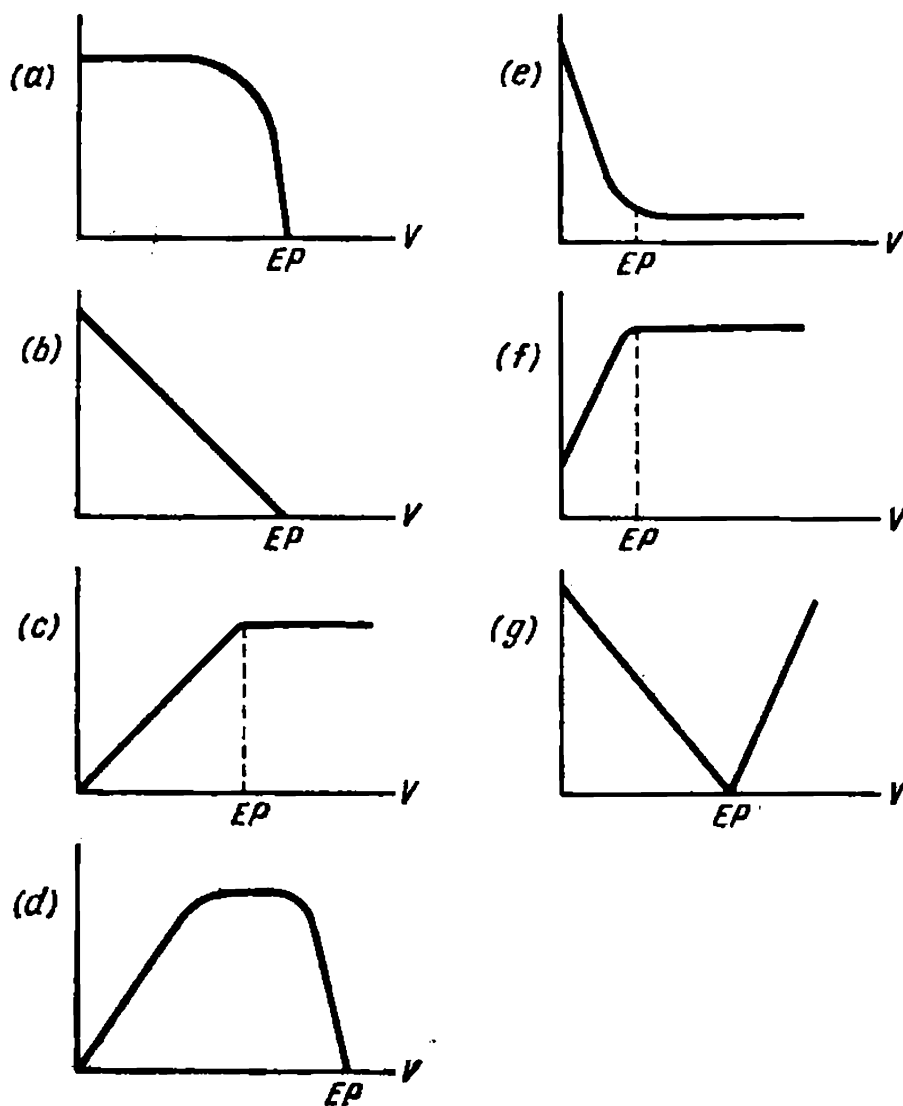


Figure 33

following answers explains correctly the energy processes taking place in these transitions?

(a) The transfer "a" involves the evolution of energy as heat.

(b) The transition "h" involves the liberation of an absorbed energy quantum in the form of a radiation of the same frequency. Such transitions are hardly probable.

(c) The transfer "e" occurs in two stages. First, the heat energy is evolved and then the energy in the form of luminescent radiation.

(d) The transitions “c”, “e”, and “f” take place in several stages, each of which involves the evolution of radiant energy in the form of luminescent radiation.

(e) The transitions “c” and “f” involve the evolution of heat energy when electrons are transferred within the con-

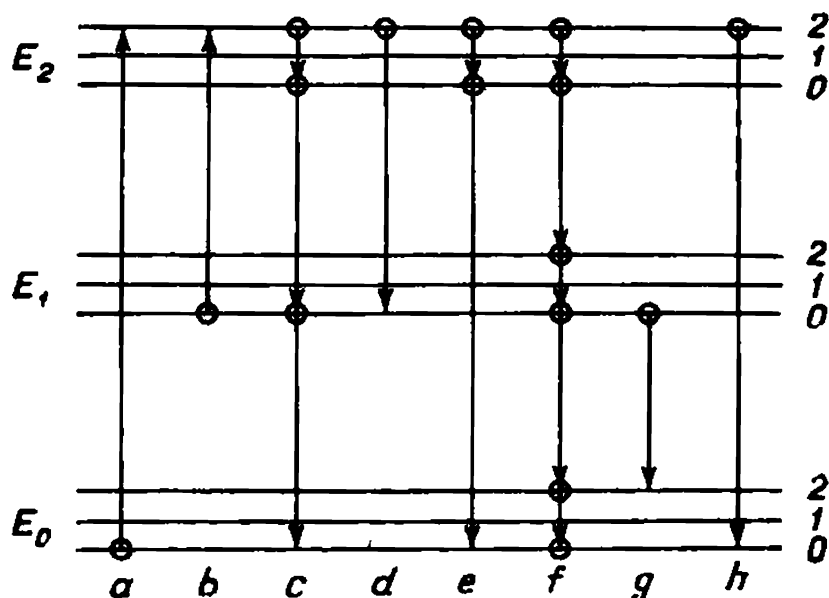


Figure 34

finer of one level, and radiant energy in the form of luminescence when the electrons are transferred from one level to another.

(f) Of all the electron transfers given only the transition “e” involves luminescent emission, the magnitude of the quantum of absorbed energy being higher than that of the quantum of radiant energy.

(g) In “c”, “e”, and “f”, the transfer of electrons from one sublevel to another involves a weak luminescent emission, and in transitions from one level to another heat energy is evolved.

(h) The transitions “d” and “g” are accompanied by the emission of a strong luminescence.

3. ASSIGNMENTS ON OPTICAL METHODS OF ANALYSIS FOR TEACHING MACHINES

FIRST ASSIGNMENT. Work up the theory of the colorimetric method of analysis.

Main question. What form will the Bouguer-Lambert-Beer equation assume with the dependence of the absorption on

the temperature and pH of the solution being taken into account if there is a linear relation between absorption, temperature and pH in the range being examined?

Indicate the correct answer.

$$(1) I_{\tau} = I_0 e^{-\epsilon l C} (1 + \alpha t) (1 + \beta \text{pH}).$$

$$(2) D = \epsilon l C (1 + \alpha t) (1 + \beta \text{pH}).$$

$$(3) I_{\tau} = I_0 \times 10^{-\epsilon l C t \text{ pH}}.$$

$$(4) \log I_0 - \log I_{\tau} = \epsilon l C (1 + \alpha t + \beta \text{pH}).$$

If your answer is correct, pass over to the next assignment.

If your answer is incorrect, give an answer to the first additional question.

First additional question. Write the equation for the Bouguer-Lambert-Beer law and the equations relating the molar extinction coefficient to the temperature and pH and compare with the answers given:

$$(5) I_{\tau} = I_0 e^{-\epsilon l C}; \quad \epsilon_t = \epsilon_0 \alpha t; \quad \epsilon_{\text{pH}} = \epsilon_0 \beta \text{pH}.$$

$$(6) I_0 = I_{\tau} \cdot 10^{-\epsilon l C}; \quad \epsilon_t = \epsilon_0 + \alpha t; \quad \epsilon_{\text{pH}} = \epsilon_0 + \beta \text{pH}.$$

$$(7) I_{\tau} = I_0 \cdot 10^{-\epsilon l C}; \quad \epsilon_t = \epsilon_0 (1 + \alpha t); \quad \epsilon_{\text{pH}} = \epsilon_0 (1 + \beta \text{pH}).$$

If your answer is correct, pass over to the second additional question.

If your answer is incorrect, work up the material again.

Second additional question. What equation can be used to express the relation between the molar extinction (absorption) coefficient and the temperature and pH?

Indicate the correct answer.

$$(8) \epsilon_{t, \text{pH}} = \epsilon_0 (1 + \alpha t) (1 + \beta \text{pH}).$$

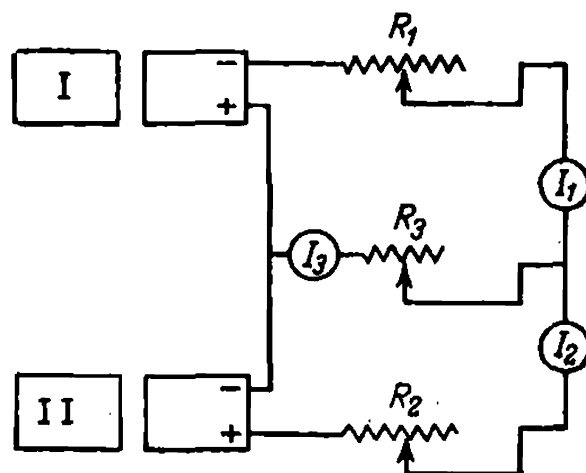
$$(9) \epsilon_{t, \text{pH}} = \epsilon_0 t \text{pH}.$$

$$(10) \epsilon_{t, \text{pH}} = \epsilon_0 (1 + \alpha t + \beta \text{pH}).$$

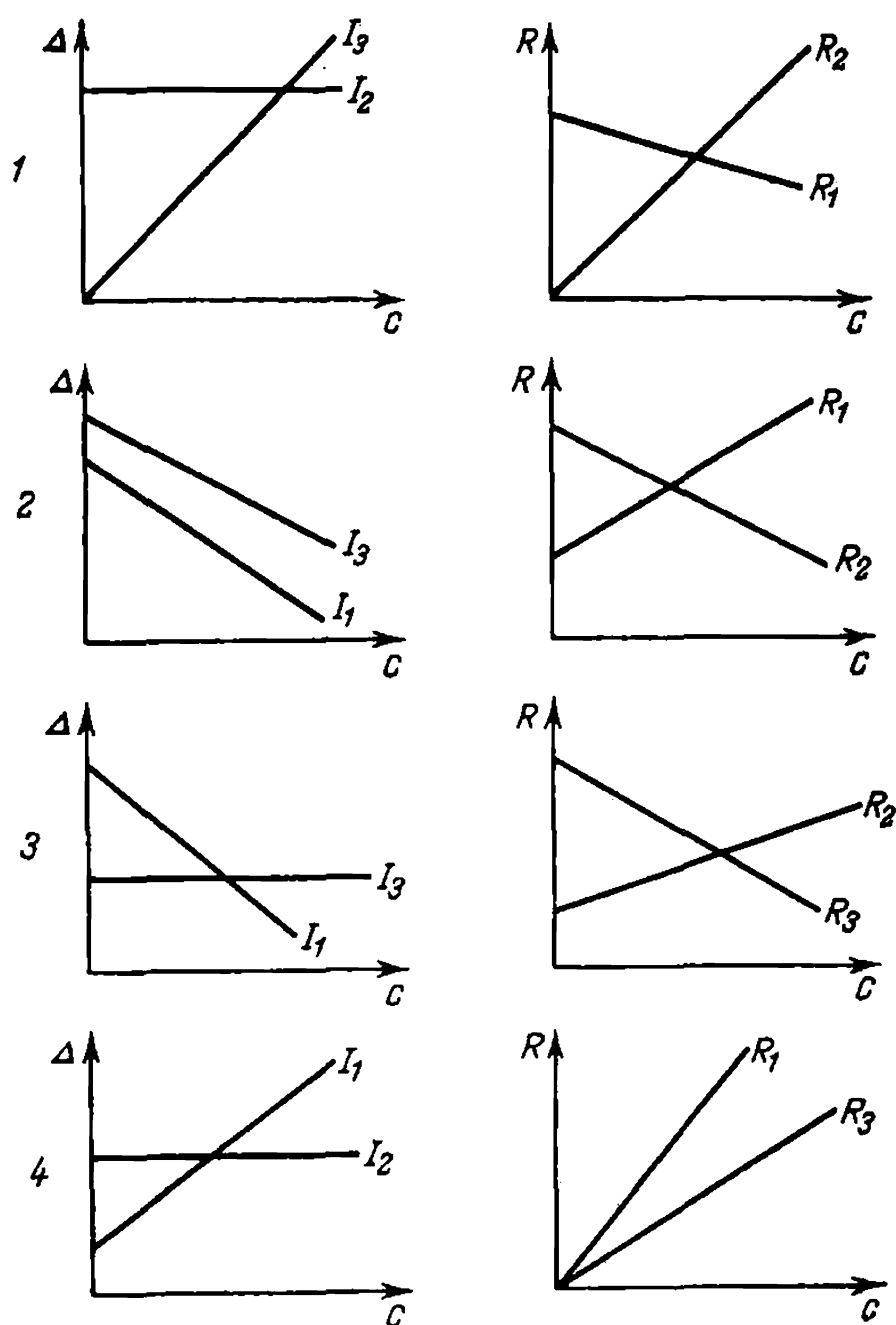
If your answer is correct, pass over to the third additional question.

If your answer is incorrect, recapitulate the section of mathematics "Investigation of functions of several variables".

Third additional question. Take logarithms of the Bouguer-Lambert-Beer equation and introduce into it the equation



(a)



(b)

Figure 35

expressing the dependence of the molar extinction coefficient on temperature and pH.

Give the correct answer to the main question.

SECOND ASSIGNMENT. Work up the section on the design of photoelectric colorimeters and rules for working with them.

Main question. A differential photoelectric colorimeter (photometer) is assembled according to the block diagram shown in Fig. 35a. The background solution is placed in cuvette *II* and coloured solutions are poured into cuvette *I*, gradually increasing their concentration. How will the readings of all the galvanometers change? How must the resistances of the rheostats be changed for the readings of the third galvanometer I_3 to remain unchanged? Compare your answer with the graphs shown in Fig. 35b.

If your answer is correct, pass over to the next assignment.

If your answer is wrong, give an answer to the first additional question.

First additional question. Specify the change of the photocurrents in parts *I* and *II* of the photometer and indicate the course of the diagonal. What will occur in them if the photocurrent in the first circuit is changed as the concentration of the coloured solution in the first cuvette increases?

Indicate the correct answer.

5. i_1 decreases, while i_2 remains unchanged, and $i_3 = i_1 + i_2$ decreases.

6. i_1 increases, i_2 decreases, and $i_3 = i_1 - i_2$ increases.

7. i_1 decreases, i_2 remains unchanged, and $i_3 = i_2 - i_1$ increases.

If your answer is correct, pass over to the second additional question.

If your answer is wrong, work up the material again.

Second additional question. How must the resistance of the rheostat be changed for the current in the diagonal to be kept constant?

Indicate the correct answer.

8. R_1 and R_3 must be increased and R_2 decreased.

9. R_3 must remain unchanged and R_2 and R_1 increased.

10. R_1 must be decreased, R_2 increased, and R_3 kept unchanged.

If your answer is correct, give an answer to the main question. And if your answer is incorrect, recapitulate Ohm's law and then answer this question.

THIRD ASSIGNMENT. To control the coloured solutions in three cuvettes a circuit is made up, which is shown in Fig. 36.

Main question. How will the readings of the galvanometer change with increasing concentration of the solutions in the

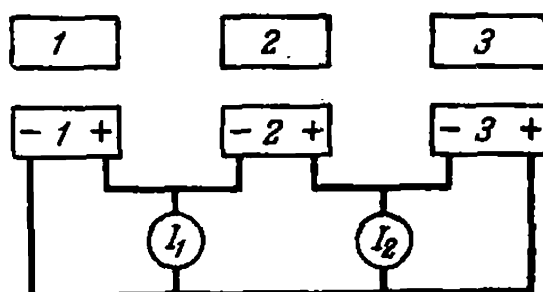


Figure 36

cuvettes? At the beginning of the experiment the photocurrent i_2 is higher than i_1 and i_3 .

Compare your answer with the graphs shown in Fig. 37.

If your answer is correct, pass over to the next assignment. In case your answer is incorrect, give an answer to the first additional question.

First additional question. Draw up a diagram showing the passage of the photocurrents and check which of the formulas given below is correct:

$$4. C_1 = k(i_2 - i_1); \quad C_2 = k(i_1 - i_2); \quad C_3 = k(i_2 - i_3).$$

$$5. C_1 = ki_1; \quad C_2 = ki_2; \quad C_3 = ki_3.$$

$$6. C_1 = k \frac{i_1}{i_2}; \quad C_2 = k \frac{i_2}{i_1}; \quad C_3 = k \frac{i_3}{i_2}.$$

If your answer is correct, give an answer to the second additional question. In case your answer is wrong, recapitulate the section on the design of photoelectric colorimeters in your textbook.

Second additional question. Assuming that at the beginning of the experiment all the currents are compensated, give an answer to the main question.

FOURTH ASSIGNMENT. Work up the theory of the refractometric method.

Main question. Show graphically the dependence of the molecular refraction R on the refractive index n , the density d , and the molecular weight M , assuming alternately

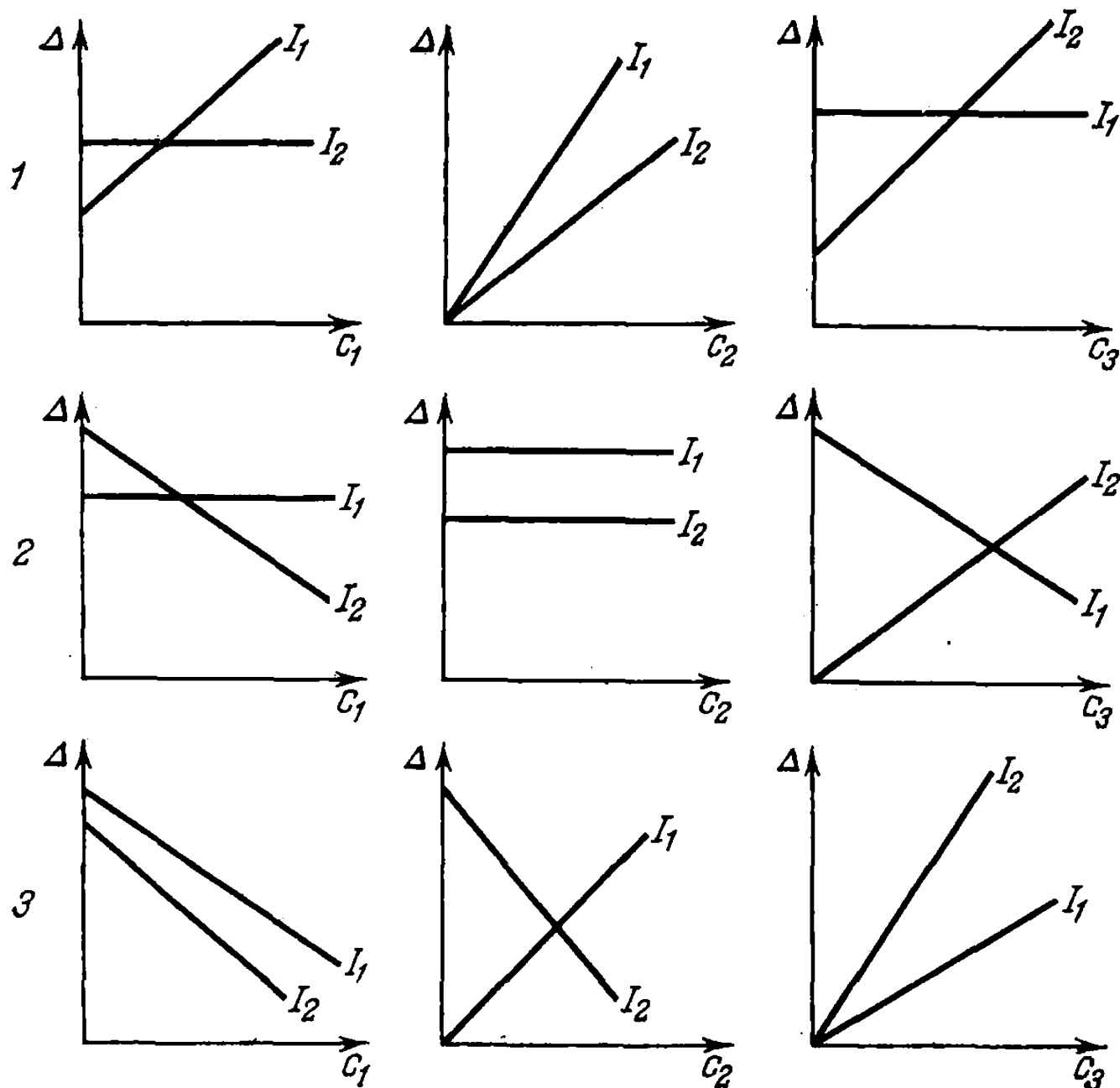


Figure 37

that one of the parameters is constant. (The subscript 1 on the graphs refers to the lower value of the parameter.) Compare your answer with the graphs in Fig. 38. If your answer is incorrect, answer the first additional question.

First additional question. Write down the formula for calculating the molecular refraction and derive the equation expressing its dependence on M , d , and n , assuming that one of the parameters is constant. When expressing the dependence of R on n , suggest an equation in which n would be included either in the denominator or the numerator

of the fraction. How will the value of R change at different values of n : 1, 1.2, 1.4, 1.6, 1.8, 2.0 (see Table 18, p. 142)?

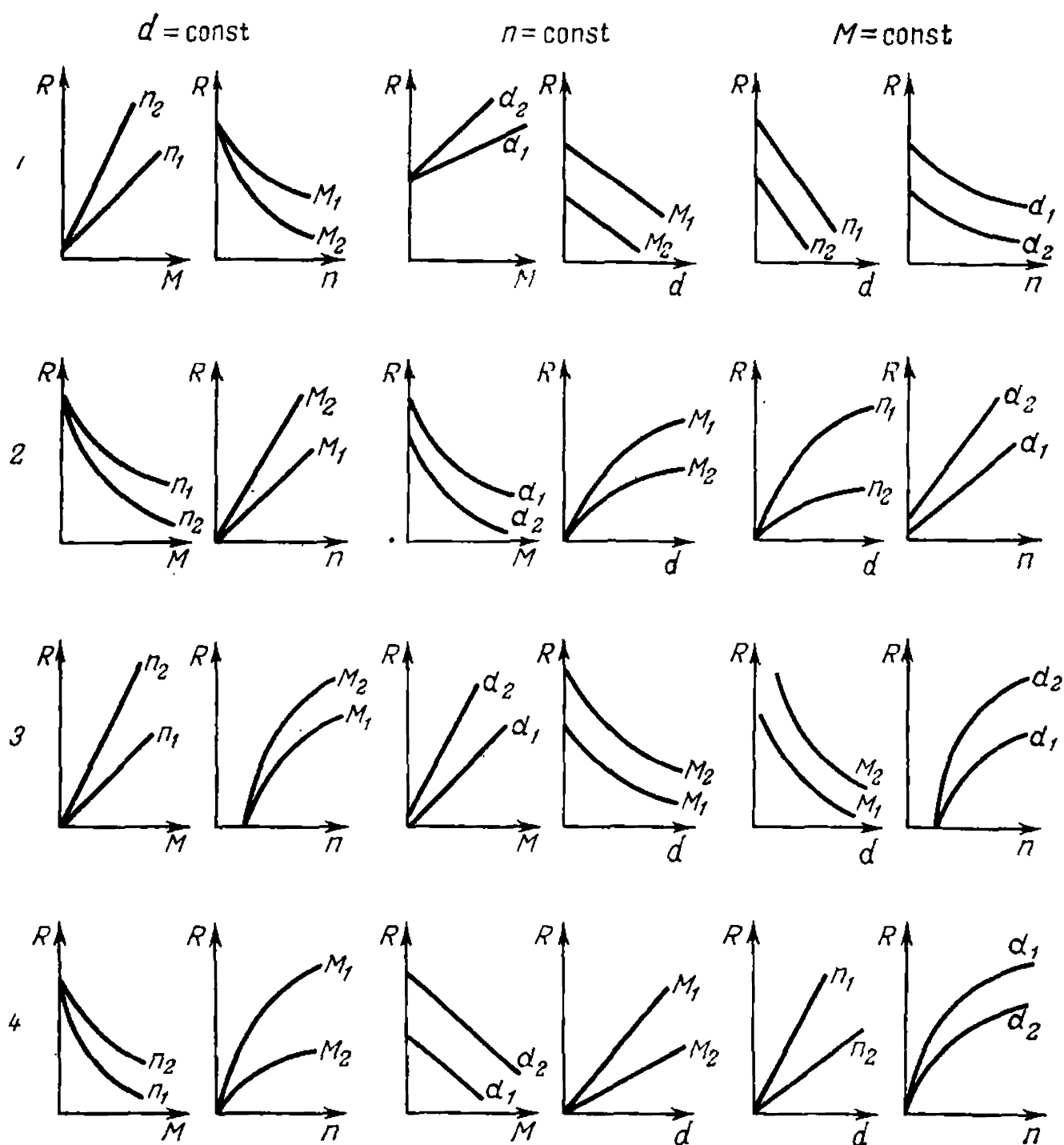


Figure 38

If your answer is correct, give an answer to the second additional question. In case your answer is wrong, recapitulate the theory of refractometry and the section of mathematics on the graphical representation of functional dependences.

Second additional question. Consider the manner in which the coefficient of the equations chosen in answering the first additional question depends on the constant param-

ter K . Show this dependence graphically and compare the answer with Fig. 39.

If your answer is correct, give an answer to the main question.

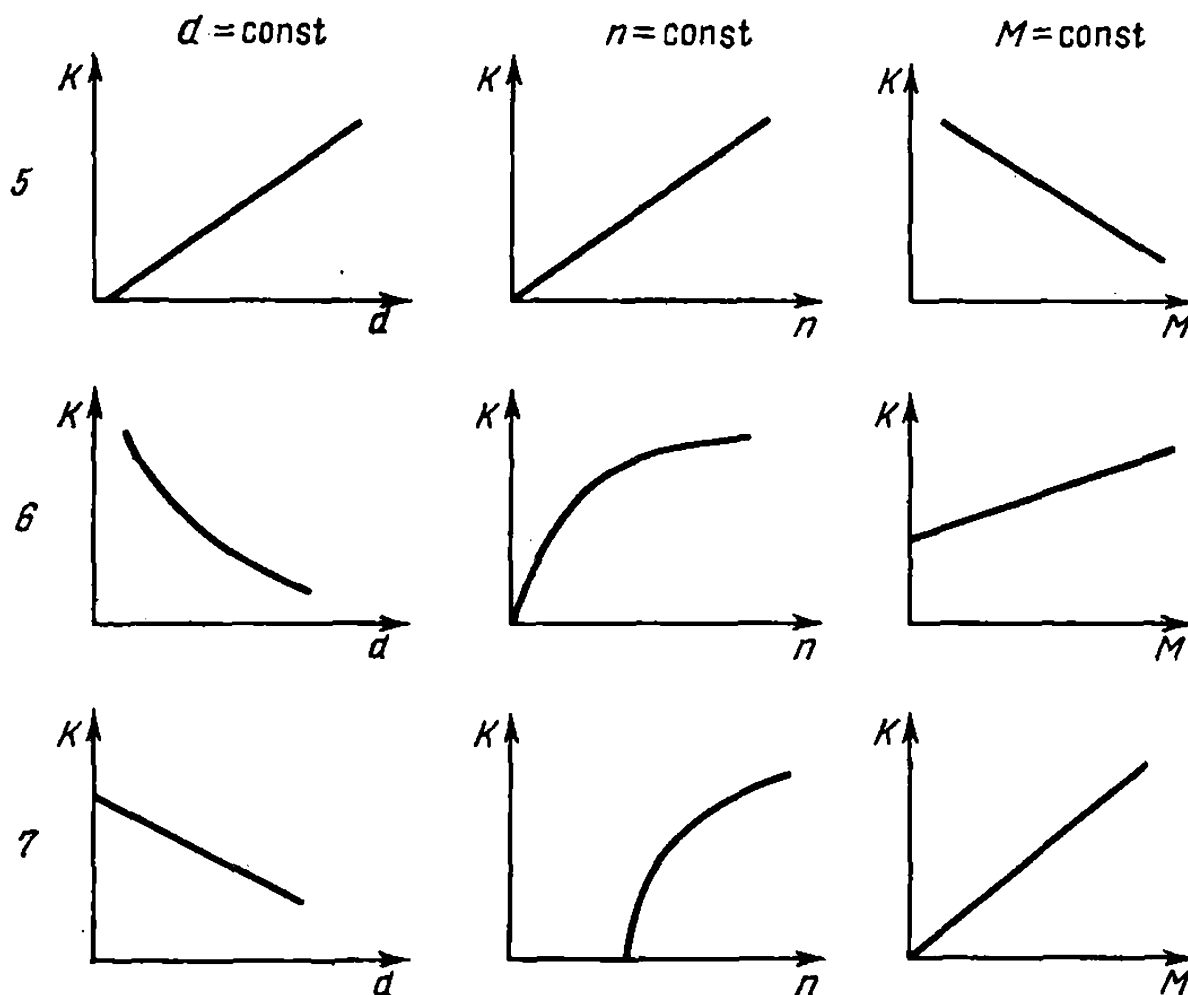


Figure 39

In case your answer is wrong, recapitulate the section of mathematics on the graphical representation of functional dependences and turn back to the first additional question.

TABLE 18

| | $d = \text{const}$ | $n = \text{const}$ | $M = \text{const}$ |
|----|---|-------------------------------|---|
| 8 | $R = KMn^2$ | $R = K \frac{M}{d}$ | $R = K \frac{n}{d}$ |
| 9 | $R = KM \left(1 - \frac{3}{n^2 + 2}\right)$ | $R = K \frac{M}{d}$ | $\frac{1}{R} = Kd \left(1 + \frac{3}{n^2 - 1}\right)$ |
| 10 | $\frac{1}{R} = K \frac{1}{M} (n^2 - 1)$ | $\frac{1}{R} = K \frac{d}{M}$ | $R = K \frac{n^2}{d}$ |

Spectroscopy *

The problems in this chapter are, as in Chapter VI, of two types: A and B.

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. Calculate the wavelength of the resonance line of the sodium atom if the excitation energy of the resonance level is 2.1 eV.

Solution: The wavelength λ (in nm) is equal to

$$\lambda = \frac{hc}{\Delta E} = \frac{12,330}{2.1} = 587.2 \text{ nm}$$

where ΔE is the difference in the potentials of the ground and excited states, eV; h is Planck's constant, and c is the velocity of light (in vacuum).

Example 2. Calculate the distance l between the lines of the principal component of an alloy and the unknown impurity on the focal plane of the optical spectral instrument if the inverse linear dispersion of the instrument is $D = 1.3 \text{ nm/mm}$ and the wavelengths of the lines are respectively 410.4 and 410.2 nm.

Solution: The distance between the lines, l , is

$$l = \frac{\partial l}{\partial \lambda} \cdot \Delta \lambda = \frac{\Delta \lambda}{D}$$

$$\Delta \lambda = 410.4 - 410.2 = 0.2 \text{ nm}$$

Hence

$$l = \frac{0.2 \text{ nm}}{1.3 \text{ nm/mm}} = 0.154 \text{ mm}$$

* This chapter was written by L. S. Lomonosova.

Example 3. Determine the permissible maximum widths of the entrance and exit slits (b_{ent} and b_{exit}) of a quantometer, which make it still possible to avoid overlapping of the spectral line of the background on the line of the minor impurity of silver in an analysis of pure copper using a direct-current arc. It is assumed that there are no other lines between the lines of the background and silver in the spectrum of the sample. The inverse linear dispersion of the instrument is $D = 1.3$ nm/mm, and the magnification of the instrument is 1.4.

Solution: We find the slit sizes:

$$b_{\text{exit}} = \Delta\lambda \cdot \frac{\partial l}{\partial \lambda} = \frac{\Delta\lambda}{D}$$

$$b_{\text{exit}} = \beta b_{\text{ent}}$$

where $\Delta\lambda$ is the difference of the wavelengths of the silver and copper lines, in nm; β is the linear magnification of the instrument.

By reference to the tables of spectral lines we find the "last" line of silver $\lambda_{\text{Ag}} = 328.068$ nm and the line of copper $\lambda_{\text{Cu}} = 327.396$ nm.

Hence

$$\Delta\lambda_{\text{Ag, Cu}} = 328.068 - 327.396 = 0.672 \text{ nm}$$

$$b_{\text{exit}} = \frac{0.672}{1.3} = 0.52 \text{ mm}$$

$$b_{\text{ent}} = \frac{0.52}{1.4} = 0.37 \text{ mm}$$

Example 4. In the spectrum of a sample there is one more line between the iron lines $\lambda_1 = 304.266$ nm and $\lambda_2 = 304.508$ nm.

Calculate the wavelength of this line, λ_x , if on the screen of the spectrum projector it is 1.5 mm away from the first line of iron and 2.5 mm away from the second.

Solution: We find λ_x :

$$\lambda_x = \lambda_1 + (\lambda_2 - \lambda_1) \frac{l_x}{l}$$

where l_x is the distance between the first iron line and the unknown line, and l is the distance between the known lines of iron.

Substituting the data given, we get:

$$\lambda_x = 304.266 + (304.508 - 304.266) \frac{1.5}{4.0} = 304.357 \text{ nm}$$

Example 5. Plot a calibration graph and use it for determining the content of antimony in lead on the basis of the measured values of blackening of the analytical lines in the spectra of the standards and the unknown sample (see Table 19).

TABLE 19

| Sample | Concentration of antimony, per cent | log C | Blackening of analytical lines | | | | |
|----------|-------------------------------------|-------|--------------------------------|-----------------|-----------------|------------|------------------|
| | | | spectrum No. | S _{Sb} | S _{Pb} | calculated | |
| | | | | | | ΔS | $\Delta \bar{S}$ |
| Standard | 0.12 | -0.92 | 1 | 0.81 | 1.61 | -0.80 | — |
| | — | — | 2 | 0.67 | 1.45 | -0.78 | — |
| | — | — | 3 | 0.85 | 1.63 | -0.78 | -0.79 |
| | — | — | 4 | 0.78 | 1.58 | -0.80 | — |
| | — | — | 5 | 0.82 | 1.61 | -0.79 | — |
| | 0.38 | -0.42 | 1 | 1.24 | 1.58 | -0.34 | — |
| | — | — | 2 | 1.17 | 1.52 | -0.35 | — |
| | — | — | 3 | 1.21 | 1.56 | -0.35 | -0.35 |
| | — | — | 4 | 1.20 | 1.55 | -0.35 | — |
| | — | — | 5 | 1.19 | 1.56 | -0.37 | — |
| | 1.25 | 0.10 | 1 | 1.62 | 1.58 | +0.04 | — |
| | — | — | 2 | 1.56 | 1.49 | +0.07 | — |
| | — | — | 3 | 1.72 | 1.68 | +0.06 | +0.06 |
| | — | — | 4 | 1.63 | 1.58 | +0.05 | — |
| | — | — | 5 | 1.72 | 1.66 | +0.06 | — |
| Unknown | C | — | 1 | 1.00 | 1.57 | -0.57 | — |
| | — | — | 2 | 1.05 | 1.70 | -0.65 | -0.62 |
| | — | — | 3 | 1.10 | 1.73 | -0.63 | — |
| | — | — | 4 | 0.98 | 1.61 | -0.63 | — |
| | — | — | 5 | 0.95 | 1.59 | -0.64 | — |

Solution: We determine $\Delta\bar{S}$ (see Table 19) from data on S_{Sb} and S_{Pb} and plot a calibration graph in the coordinates $\Delta\bar{S}$ versus $\log C$ (see Fig. 40) and find, from the graph,

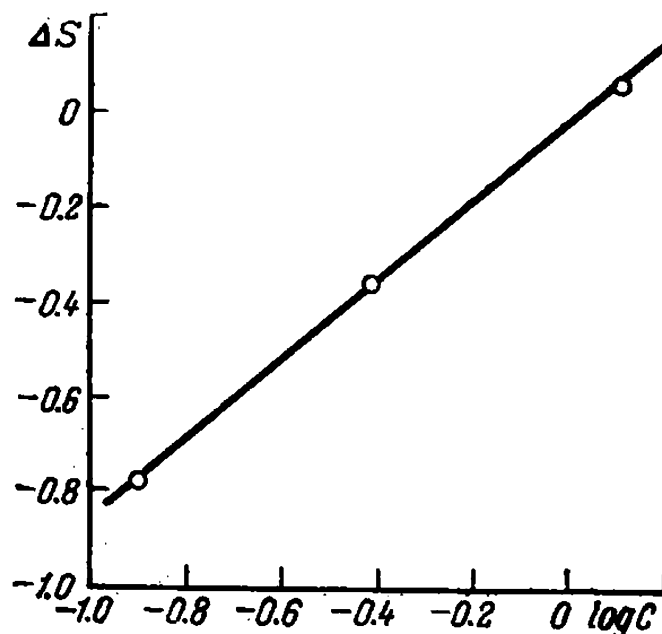


Figure 40

that at $\Delta\bar{S} = -0.62$ the value of $\log C = -0.72$; hence the result of the analysis is 0.19 per cent.

Solve the problem in the coordinates S versus $\log C$ and compare the selected dispersion of the measurement of the concentration with respect to $\Delta\bar{S}$ and S .

2. MULTIVARIANT PROBLEMS

1. Determine the wavelength of the resonance line in the atomic spectra of the elements listed below from the energy of the resonance level:

| | | | | | | | | |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|-------|
| Variant | I | II | III | IV | V | VI | VII | VIII |
| Element | K | Li | La | Cu | Rb | Be | Sb | Ne |
| Excitation energy, eV | 1.6 | 1.9 | 2.5 | 3.8 | 4.4 | 5.3 | 6.0 | 16.79 |

2. Determine the wavelengths of the analytical lines in the optical and atomic spectra of the following elements from the energies of the upper and lower levels:

| | | | | | | | | |
|---------------------------|------|------|------|------|-----|-------|-------|------|
| Variant | I | II | III | IV | V | VI | VII | VIII |
| Element | H | H | Li | Li | Li | Ne | Ne | Hg |
| Energy of upper level, eV | 12.1 | 12.7 | 3.9 | 4.5 | 3.8 | 18.9 | 18.6 | 6.67 |
| Energy of lower level, eV | 10.2 | 10.2 | 1.84 | 1.84 | 0 | 16.79 | 16.57 | 0 |

3. It is necessary to determine by optical spectral analysis the minimum content of the impurities of the listed elements in the samples in variants I-V.

| | | | |
|-------------|----------------|--------------|--------------------|
| I | Pb, S, Fe | IV | H, O, N |
| II | Cu, Ni, Mn, Mg | V | Si, Fe, Al, Mo, As |
| III | Mn, Mg, Si, P | | |

Indicate the spectral range of the instrument that permits recording simultaneously the analytical lines of the optical spectra of these elements.

Name the models of instruments suitable for this analysis.

4. Determine the distance between the spectral lines indicated below on the focal plane of a spectral instrument from their wavelengths and the inverse dispersion of the instrument:

| | | | | | | | |
|--|-------|-------|-------|---------|---------|--------------------|---------|
| Variant | I | II | III | IV | V | VI | VII |
| Wavelength, nm | | | | | | | |
| λ_1 | 327.4 | 327.4 | 327.4 | 425.078 | 427.878 | 425.078 | 510.554 |
| λ_2 | 328.0 | 328.0 | 328.0 | 425.433 | 425.433 | 425.433 | 510.890 |
| Inverse linear dispersion, nm/mm . . . | 1.3 | 0.4 | 10.0 | 4 | 6 | (a) 4.2 (b) 1.9 | 4.2 |

5. Calculate the wavelength of the unknown line from the wavelengths of two base lines of the comparison spectrum and from the distances between the lines, on the screen of the spectrum projector; calculate the position of the known lines with respect to the base lines:

| | | | | | | | |
|----------------------------|---------|---------|---------|---------|---------|---------|---------|
| Variant | I | II | III | IV | V | VI | VII |
| Base lines | | | | | | | |
| first wave-length, nm . . | 275.358 | 275.358 | 347.545 | 272.358 | 640.803 | 402.187 | 402.187 |
| position reading, mm | 0 | 0 | 9.5 | 0 | 20 | 58.0 | 0 |
| second wave-length, nm . . | 272.09 | 272.09 | 346.644 | 272.09 | 641.166 | 402.474 | 402.474 |
| position reading, mm | 20 | 20 | 51 | 10 | 28.5 | 72.0 | 14 |

Unknown
line

wave-
length,

nm . . 272.256 271.902 x 272.56 x 402.30 x

position

reading,

mm x x 87 x 27 x 8.5

6. Determine the maximum permissible width of the entrance and exit slits of a monochromator or quantometer that enables the overlapping of nearest neighbouring lines to be avoided under the following conditions:

| | | | | |
|---|---------|---------|---------|---------|
| Variant | I | II | III | IV |
| Length of lines, nm | | | | |
| first | 404.763 | 404.763 | 404.763 | 404.763 |
| second | 404.598 | 404.598 | 404.598 | 404.598 |
| Inverse linear dispersion, nm/mm | 10.0 | 10.0 | 0.83 | 0.6 |
| Variant | V | VI | VII | VIII |
| Length of lines, nm | | | | |
| first | 404.763 | 231.096 | 231.096 | 231.096 |
| second | 404.598 | 231.147 | 231.147 | 231.147 |
| Inverse linear dispersion, nm/mm | 0.83 | 0.6 | 0.6 | 0.83 |

TABLE 20

| Sample | C, % | S_{Ag} | S_{Cu} | $\Delta S_{Ag, Cu}$ |
|----------|-------|----------|----------|---------------------|
| Standard | 0.18 | 0.41 | 0.64 | — |
| | | 0.42 | 0.67 | — |
| | 0.23 | 0.45 | 0.66 | — |
| | | 0.46 | 0.65 | — |
| | 0.34 | 0.51 | 0.64 | — |
| | | 0.52 | 0.65 | — |
| | 0.40 | 0.55 | 0.65 | — |
| | | 0.55 | 0.63 | — |
| | 0.55 | 0.67 | 0.65 | — |
| | | 0.69 | 0.69 | — |
| Unknown | C_1 | 0.50 | 0.65 | — |
| | | 0.52 | 0.66 | — |
| | C_2 | 0.49 | 0.66 | — |
| | | 0.46 | 0.64 | — |
| | C_3 | — | — | —0.18 |
| | C_4 | — | — | —0.20 |
| | | — | — | +0.01 |
| | | — | — | —0.03 |

By reference to tables of spectral lines determine the elements having in their spectra the lines indicated in variants I-V and VI-VIII.

7. Plot the calibration curves and use them to determine the content of silver in copper castings and the content of manganese in steel components on the basis of the measured blackenings of the analytical lines in the spectra of the unknown and standard samples listed in Tables 20 and 21.

TABLE 21

| Sample | C, % | log C | S_{Mn} | S_{Fe} | $\Delta S_{\text{Mn, Fe}}$ | $\Delta \bar{S}_{\text{Mn, Fe}}$ |
|----------|-------|-------|-----------------|-----------------|----------------------------|----------------------------------|
| Standard | — | —0.20 | — | — | — | —0.05 |
| | — | —0.30 | — | — | — | —0.18 |
| | — | —0.42 | — | — | — | —0.25 |
| | — | —0.50 | — | — | — | —0.40 |
| Unknown | C_5 | — | 0.68 | 0.80 | — | — |
| | — | — | 0.67 | 0.80 | — | — |
| | C_6 | — | 0.55 | 0.79 | — | — |
| | — | — | 0.53 | 0.80 | — | — |
| | C_7 | — | — | — | —0.15 | — |
| | — | — | — | — | —0.16 | — |
| | C_8 | — | — | — | —0.29 | — |
| | — | — | — | — | —0.28 | — |

Table 20 presents data to be used for determination of silver in copper.

Table 21 gives data to be used for determination of manganese in steel.

3. PROBLEMS

SECTION A

1. An optical instrument is fitted with two interchangeable cameras with focal lengths of 120 and 270 mm.

What will be the change of the linear dispersion and magnification of the instrument if the first camera is replaced by the second?

Compare the relative position of two neighbouring spectral lines in the spectra obtained with the first and the second camera, other conditions being identical, if the lines in the spectrum obtained with the camera having $f_1 = 120$ mm touch and do not touch each other.

2. An instrument is equipped with a diffraction grating which makes it possible to obtain sufficiently intensive spectra of the first three orders.

What region of the spectrum must a light filter placed in front of the entrance slit pick up to prevent the overlap of the second-order spectrum on the 410-650.0 nm region of the first-order spectrum and of the spectra of the two other orders on the 250-350 nm region of the second-order spectrum.

3. How many spectrograms can a photographic plate 9 cm wide contain if the illuminated area of the slit is 1 mm high, the magnification of the spectrograph is 1.2, and the edges of the holder cover the plate on both sides by 5 mm (the distance between the spectra is to be ignored)?

4. Estimate the extent to which the luminosity of the collimator is used if the working surface of the light source is 5×5 mm², the distance between the source and the entrance slit of the instrument is 120 mm, and the ratio d/f^* (called the lens aperture ratio) is 50 mm/600 mm.

How far away should the light source be placed from the slit for the collimator to be completely "filled" with light passing through the central point of the slit?

5. The blackening of an analytical line in the spectrum of a standard with the highest concentration of the element to be determined is 0.5 when the collimator is filled with the light from the working part of the light source and the exposure time is 15 seconds. Since this blackening is close to the underexposure region, it is desirable to increase the blackening of the analytical line in the spectrum of the indicated standard to 1.5.

How many times must the exposure time be increased if the contrast factor of the photoemulsion plate is 1, the width of the emulsion is 0.4-1.9 and the intensity of the analytical line is constant in time.

* d is the camera lens diameter and f is its focal length.—*Tr.*

How many times should the aperture ratio be increased in order to achieve, with the same plates, a blackening of 1.5 provided that the element being determined is exhausted completely in 15-20 sec.

6. At a voltage of 1000 V supplied to a photomultiplier the photocurrent from the analytical line assumed the values from 1 to 10 μA depending on the concentration of the element being determined. The 10 μA current is the permissible limit for this photomultiplier.

How many times must the area of the entrance slit of a spectral instrument or the voltage fed to the photomultiplier be reduced in order to lower the photocurrent to 0.1-1 μA . The sensitivity of the photomultiplier is: 10 A/lm at a voltage of 600 V, 100 A/lm at 800 V, and 100 A/lm at 1010 V. (Assume that there is no background and that the photocurrent varies linearly with the magnitude of the light beam.)

7. To identify the samples of wire steel use was made of a steeloscope and the analytical data presented in Table 22.

TABLE 22

| Chromium | | Nickel | |
|----------------------------|---------------------------------|----------------------------|---------------------------------|
| concentration, per cent | intensity of Cr and Fe lines | concentration, per cent | intensity of Ni and Fe lines |
| 0.1 | Cr 520.84 = Fe 520.23 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 0.2 | Cr 520.45 = Fe 520.23 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 0.3 | Cr 520.603 = Fe 520.23 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 0.45-0.75 | Cr 427.49 < Fe 428.24 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 0.80-1.20 | Cr 427.49 = Fe 428.24 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 1.3-1.65 | Cr 428.97 = Fe 429.413 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 10-14 | Cr 492.226 < Fe 491.90 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 14-18 | Cr 492.226 = Fe 492.39 | 55-61 | Ni 547.69 > Fe 545.56 |
| 16-20 | Cr 492.226 = Fe 491.9 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 22-27 | Cr 492.226 > Fe 491.9 | < 0.6 | Ni 547.69 < Fe 545.56 |
| 16-20 | Cr 492.26 = Fe 491.9 | 8-15 | Ni 547.69 = Fe 545.56 |

It turned out that the samples may be divided into four groups (I-IV) according to the ratio of the intensities of analytical lines:

TABLE 23

| Standard sample | Concentration, per cent | | | | | Difference in blackening (averaged over three spectra) | | | | |
|--|-------------------------|----------|----------|----------|----------|--|---------------------------|---------------------------|---------------------------|----------|
| | Mn | Si | Mo | Cr | Ni | $\Delta \bar{S}_{Mn, Fe}$ | $\Delta \bar{S}_{Si, Fe}$ | $\Delta \bar{S}_{Mo, Fe}$ | $\Delta \bar{S}_{Ni, Fe}$ | |
| 291 | 2.00 | 0.10 | — | 0.163 | 0.72 | +0.393 | —0.345 | —0.130 | +0.136 | |
| 292 | 0.45 | 1.12 | 0.18 | 2.18 | 0.38 | —0.330 | +0.535 | +0.950 | —0.160 | |
| 293 | 0.159 | 1.51 | 0.42 | 0.845 | 0.19 | —0.720 | +0.600 | +0.480 | —0.570 | |
| 294 | 0.968 | 0.39 | 0.70 | 0.46 | 1.31 | +0.065 | +0.190 | +0.350 | +0.410 | |
| Blackening of lines (in each spectrum) | | | | | | | | | | |
| Unknown sample | S_{Mn} | S_{Fe} | S_{Si} | S_{Fe} | S_{Mo} | S_{Fe} | S_{Cr} | S_{Fe} | S_{Ni} | S_{Fe} |
| | | | | | | | | | | |
| 1 | 1.450 | 1.160 | 0.610 | 0.910 | 0.820 | 1.000 | 0.730 | 0.700 | 0.950 | 1.180 |
| | 1.400 | 1.150 | 0.615 | 0.920 | 0.880 | 1.100 | 0.690 | 0.690 | 0.980 | 1.150 |
| | 1.450 | 1.155 | 0.620 | 0.920 | 0.825 | 1.010 | 0.740 | 0.730 | 0.980 | 1.160 |
| 2 | 0.400 | 1.100 | 1.350 | 0.750 | 0.730 | 1.030 | 1.160 | 0.720 | 1.270 | 1.130 |
| | 0.420 | 1.100 | 1.300 | 0.700 | 0.750 | 1.050 | 1.100 | 0.590 | 1.280 | 1.120 |
| | 0.410 | 1.110 | 1.200 | 0.600 | 0.750 | 1.045 | 1.100 | 0.570 | 1.250 | 1.135 |

| | |
|---------------|---|
| I | Cr 520.84 = Fe 520.23; Ni 547.69 < Fe 545.56 |
| II | Cr 427.49 < Fe 428.24; Ni 547.69 = Fe 545.56 |
| III | Cr 429.226 = Fe 492.39; Ni 547.69 > Fe 545.56 |
| IV | Cr 492.26 = Fe 491.9; Ni 547.69 = Fe 545.56 |

Determine the content of Ni and Cr in these steel samples.

8. To grade two samples of steel according to the content of alloying components a standard procedure of emission spectroscopy was used, which requires that the spectrum of each sample be photographed three times. The measured values of blackening of the analytical lines are given in Table 23. The internal standards used are the line intensities of the spectrum of iron.

Determine the contents of Mn, Si, Mo, Cr, and Ni in the samples (in per cent) provided that the coefficients of variation of the method are the same for the elements and equal to ± 5 per cent.

9. To determine silver in process solutions by the atomic-absorption method from the 328.1 nm line representative samples 1 litre in volume were taken every 3 hours and evaporated to 10 ml.

Plot a graph showing the variation of the content of silver in the solutions during 24 hours from the instrument readings:

(a) for unknown samples

| | | | | | | | | |
|-------------------------|-----|-----|-----|------|-------|-------|-------|-------|
| Time period, hr | 0-3 | 3-6 | 6-9 | 9-12 | 12-15 | 15-18 | 18-21 | 21-24 |
| Instrument reading . . | 85 | 89 | 78 | 51 | 70 | 85 | 89 | 90 |

(b) for standard solutions

| | | | | | |
|---|-----|-----|-----|-----|------|
| Content of silver, $\mu\text{g/ml}$ | 0 | 0.4 | 1.0 | 2.0 | 4.0 |
| Instrument reading | 100 | 93 | 83 | 69 | 47.5 |

10. Plot a calibration graph and use it for the determination of the concentrations of chromium and manganese in two samples of ferrovanadium. The averaged values of the difference in the blackening of the analytical lines in the spectra of standards and those for the spectra of unknown samples are listed in Table 24.

Determine the percentage contents of manganese and chromium in the samples if the coefficient of variation of the method is ± 3 per cent.

11. To determine the content of oxygen in neon and helium by emission spectroscopy five spectra each of standard mixtures and unknown samples were recorded, a new portion

TABLE 24

| Sample | Concentration, per cent | | Difference in blackening of analytical lines | |
|----------|-------------------------|-------|--|----------------------------|
| | Mn | Cr | $\Delta S_{\text{Mn, Fe}}$ | $\Delta S_{\text{Cr, Fe}}$ |
| Standard | 1.26 | 1.00 | +0.46 | —0.10 |
| | 1.06 | 0.68 | +0.34 | —0.25 |
| | 1.16 | 1.29 | +0.39 | —0.04 |
| Unknown | C_1 | C_2 | +0.42 | —0.01 |
| | — | — | +0.41 | —0.01 |
| | — | — | +0.40 | —0.02 |
| | C_3 | C_4 | +0.35 | —0.155 |
| | — | — | +0.38 | —0.156 |
| | — | — | +0.35 | —0.160 |

TABLE 25

| Standard mixture | Percentage by volume of oxygen | $\Delta \bar{S}_{\text{an, av}}$ | Sample | Blackening of analytical lines | |
|------------------|--------------------------------|----------------------------------|--------|--------------------------------|--------------------|
| | | | | oxygen* | gas being analysed |

Neon ($\lambda = 783.9$ nm)

| | | | | | |
|---|---------|-------|---|------|------|
| 1 | 0.00025 | —0.10 | 1 | 0.70 | 0.55 |
| 2 | 0.0016 | +0.10 | — | 0.72 | 0.55 |
| 3 | 0.011 | +0.50 | — | 0.70 | 0.54 |
| 4 | 0.050 | +1.10 | — | 0.70 | 0.53 |
| 5 | | | — | 0.75 | 0.56 |

Helium ($\lambda = 728.1$ nm)

| | | | | | |
|---|---------|-------|---|------|------|
| 1 | 0.00032 | —1.55 | 2 | 0.80 | 1.50 |
| 2 | 0.0016 | —1.35 | — | 0.78 | 1.54 |
| 3 | 0.0030 | —1.15 | — | 0.81 | 1.56 |
| 4 | 0.011 | —0.90 | — | 0.82 | 1.57 |
| 5 | 0.10 | 0.0 | — | 0.77 | 1.50 |

* For oxygen $\lambda = 777.2$ nm.

of the gas being introduced into the discharge tube each time. Data on the blackening of the analytical lines are given in Table 25. The coefficient of variation of the analytical method for one spectrum is 15 per cent,

Determine the percentage content of oxygen in each sample.

12. To determine indium in solutions use was made of the flame photometry. The traces of the analytical line in the

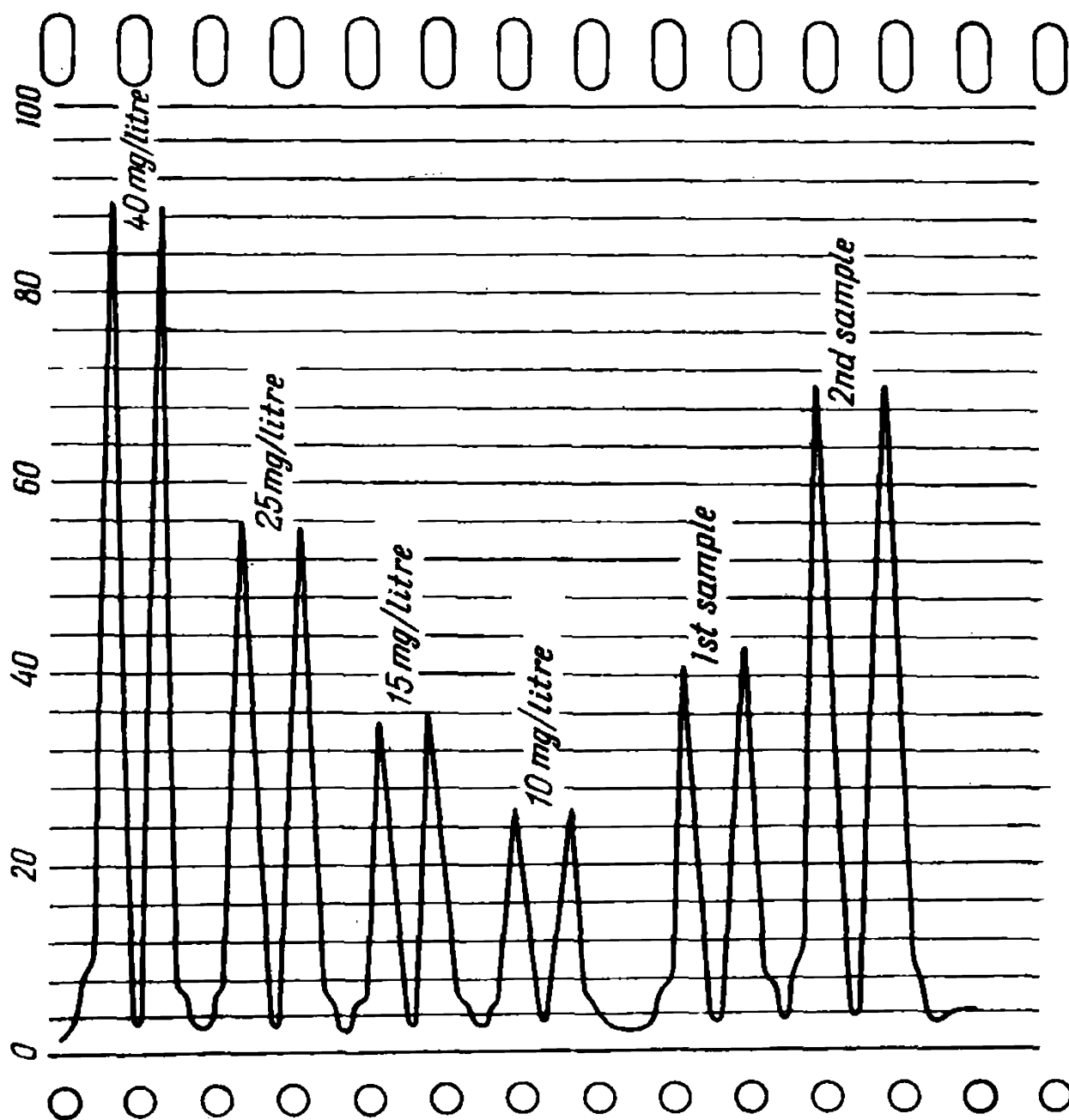


Figure 41

spectra of standards and two samples are presented in Fig. 41.

What is the result of the analysis?

13**. Rock samples were analysed with the aid of a quantometer (the results are given in Table 26).

Determine the percentage contents of Mn, Mg, and Ca.

TABLE 26

| Sample | Concentration, per cent | | | Instrument reading | | |
|----------|-------------------------|-------|-------|--------------------|------|------|
| | Mn | Mg | Ca | Mn | Mg | Ca |
| Standard | 0.018 | 0.18 | 0.40 | 11 | 0 | —38 |
| | 0.040 | 0.4 | 1.00 | 20 | 20 | —18 |
| | 0.10 | 0.75 | 4.0 | 33 | 35 | +10 |
| | 0.50 | 2.00 | — | 55 | 63 | — |
| Unknown | C_1 | C_2 | C_3 | 22.3 | 17.5 | +6.5 |

SECTION B

14**. What spectral characteristic must a light filter have to make possible the elimination of the overlap of the lines of the main component and impurities on the analytical line of lead ($\lambda = 283.3$ nm)?

15**. The system of energy levels of the neutral mercury atom contains, in particular, terms with the excitation energies $E_1 = 4.88$, $E_2 = 6.67$, $E_3 = 7.73$, and $E_4 = 8.85$ eV, and that of the neutral sodium atom, terms with $E_1 = 2.1$ and $E_2 = 4.12$ eV.

Determine the ratio N_{ex}/N_0 , i.e., the fraction number of neutral atoms of these elements which are in the indicated excited states: in a d-c arc ($T = 7000$ °K), in the flare of a condensed spark ($T = 10\,000$ °K), and in the flame of a mixture of propane, butane, and air ($T = 2200$ °K).

Plot graphs showing the dependence of the ratio N_{ex}/N_0 on the temperature of the light source and on the excitation energy of the line at the temperature of the flame and of the spark flare.

16. What resolving power must a photographic emulsion have in working with instruments with a reciprocal linear dispersion of 0.6 nm/mm (other conditions of recording being identical) for two lines of equal intensity, 410.2 and 410.24 nm, to be resolved?

17**. Figure 42 shows the dependence of the atomic absorption coefficient of iron on the wavelength in the X-ray region of the spectrum.

Will the change of the iron content in alloys of complicated composition affect the calibration curves for determination of copper and nickel?

18. At first the spectrum of an alloy was recorded with a spectrograph without the use of illuminating lenses under the following conditions: the light source was a condensed spark with a spacing of the electrodes of 5 mm, the distance between the light source and the instrument slit, 200 mm, the slit width 0.01 mm, the focal length 600 mm, the exposure time 30 seconds. The blackening of the analytical line of Sb (252.8 nm) in the spectrum of a standard containing the highest amount of the element being determined was 0.4 and coincided with the lower limit of the linear portion of the characteristic curve of the plate.

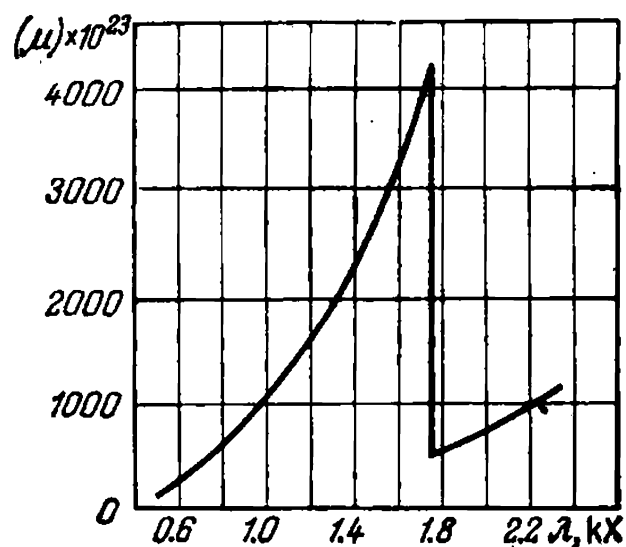


Figure 42

Suggest other conditions for photographing the spectra under which the blackenings of the analytical line for all the standards required would not go beyond the limits of the linear portion of the characteristic curve. Assume that the set of standards used corresponds to the fourfold change of the element concentration and that the analytical line does not undergo reabsorption over this range of concentrations (the operating conditions of the generator should not be changed).

19. A gas holder was filled with a hydrogen-helium mixture in several stages. The content of hydrogen in each portion was previously determined spectroscopically, taking two samples for analysis at a time. The spectra of each sample and standard gas mixtures were recorded once at a time; the results obtained are presented in Table 27.

Determine the content of hydrogen in the gas mixture (in per cent by volume).

20**. Determine the percentage of niobium in a sample of ore by the method of additions, using the following data.

The blackening of the analytical lines:

| | Nb | Ti (comparison line) |
|---|------|-------------------------|
| In the spectrum of the original sample . . | 0.59 | 0.75 |
| In the spectrum of the sample with the niobium added | | |
| 0.2 per cent | 0.91 | 0.76 |
| 0.6 per cent | 1.47 | 0.78 |

The blackening of the line steps in the spectrum recorded by using a step attenuator:

| Step | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|------|------|------|------|------|------|------|------|
| Log transmittance of the step . . . | 0.84 | 1.00 | 1.19 | 1.34 | 1.51 | 1.69 | 1.84 | 2.00 |
| Blackening of the step | 0.46 | 0.55 | 0.68 | 0.82 | 1.04 | 1.32 | 1.51 | 1.81 |

21**. Determine the percentage concentration of manganese in ferromanganese from the measured differences of the blackening of the analytical lines: Fe, 238.08; Mn, 234.88;

TABLE 27

| Gas portion | Volume, m ³ | Concentration of H ₂ , vol. % | S_{H} ($\lambda = 665.2 \text{ nm}$) | S_{He} ($\lambda = 667.0 \text{ nm}$) |
|---------------------|---------------------------|---|--|---|
| Unknown | | | | |
| 1 | 50 | C_1 | 1.85 | 0.22 |
| | | | 1.80 | 0.19 |
| 2 | 100 | C_2 | 0.95 | 0.35 |
| | | | 0.98 | 0.36 |
| 3 | 75 | C_3 | 1.30 | 0.32 |
| | | | 1.25 | 0.28 |
| 4 | 25 | C_4 | 1.15 | 0.34 |
| | | | 1.08 | 0.35 |
| Standard mixture | | | | |
| 1 | — | 0.08 | 0.80 | 0.40 |
| | | | 0.82 | 0.42 |
| 2 | — | 0.18 | 1.00 | 0.35 |
| | | | 1.05 | 0.37 |
| 3 | — | 0.42 | 1.53 | 0.31 |
| | | | 1.55 | 0.30 |
| 4 | — | 1.1 | 1.98 | 0.22 |
| | | | 1.92 | 0.20 |

Mn, 282.145; Si, 288.158. The values of $\Delta S_{\text{Fe, Mn}}$ are -0.309 and -0.311 and those of $\Delta S_{\text{Si, Mn}}$ are 0.289 and 0.281 .

The total content of C, S, P and Ca is 0.5 per cent:

| | | | |
|--------------------------------------|----------|----------|----------|
| Standard | 1 | 2 | 3 |
| Percentage content of element | | | |
| Mn | 73 | 79 | 90 |
| Fe | 25 | 18 | 9 |
| Si | 1.5 | 2.5 | 0.8 |
| Difference of blackening | | | |
| $\Delta S_{\text{Fe, Mn}}$ | -0.105 | -0.280 | -0.643 |
| $\Delta S_{\text{Si, Mn}}$ | 0.450 | 0.73 | 0.205 |

22. When working out the composition of an alloy with specified properties the control of test samples was effected by the atomic-absorption method. To do this, a weighed sample of 0.1 g was dissolved in nitric acid and the volume of the resulting solution was made up to 500 ml with distilled water. Three successive measurements were made (the results are listed in Table 28) for each standard and each unknown solution (the zero setting is 100).

TABLE 28

| Solution | Content, $\mu\text{g/ml}$ | | Instrument reading | | | | | |
|----------------|---------------------------|-------|--------------------|------|------|-------------|------|------|
| | Fe | Zn | Fe 248.3 nm | | | Zn 213.9 nm | | |
| Standards | 2 | 0.2 | 97.0 | 97.0 | 96.0 | 89.5 | 90.5 | 90.0 |
| | 5 | 0.4 | 94.0 | 93.0 | 93.5 | 84.0 | 84.0 | 84.0 |
| | 10 | 1.0 | 88.0 | 88.0 | 87.0 | 67.5 | 66.5 | 67.0 |
| | 20 | 2.0 | 75.5 | 75.5 | 75 | 50.0 | 49.5 | 49.5 |
| Unknown sample | C_1 | C_4 | 77.5 | 77.5 | 76.5 | 65.0 | 66.0 | 65.5 |
| | C_2 | C_5 | 95.0 | 96.5 | 95.5 | 84.0 | 83.5 | 84.0 |
| | C_3 | C_6 | — | — | — | — | 50.5 | 51.5 |

Find the concentrations of iron and zinc in alloys (in per cent) if the coefficient of variation of the analytical method for the averaged values of three successive measurements is equal to ± 4 per cent.

23. To determine the content of gold in a technological solution at a concentration plant the atomic-absorption

method was used. The results of the measurements of the absorption of the 242.8 nm analytical line of gold for standard solutions (the reading for a blank equals 100) are as follows:

| | | | | | |
|---------------------------------------|------|------|------|------|------|
| Concentration of Au, $\mu\text{g/ml}$ | 1 | 2 | 5 | 10 | 20 |
| Instrument reading | 95.5 | 91.5 | 81.5 | 67.0 | 48.0 |
| | 96.0 | 92.0 | 82.0 | 67.0 | 48.0 |
| | 96.0 | 92.0 | 82.0 | 67.0 | 48.0 |

The readings for the first solution of the sample are 75.0, 75.5, 74.5, and for the second solution, 52.0, 51.5, 51.0.

Determine the content of gold in the unknown solutions (in $\mu\text{g/ml}$) if the coefficient of variation of the instrument is ± 4 per cent.

Determine the sensitivity of the analyser (in $\mu\text{g/ml}$ per 1 per cent).

24**. To determine very small amounts of copper in a powder material use was made of a procedure of emission spectroscopy which requires that the sample be burned three times successively in a d-c arc; the concentration is determined from the intensity of the 324.7 nm line of copper and a "permanent" graph of $\log C$ versus $\log I_{\text{an}}$ with account taken of the background.

Determine the percentage content of copper in the sample if the blackenings of the line and the background in the spectra of the samples are as follows:

| | | | |
|-------------------------|------|------|------|
| Spectrum No. | 1 | 2 | 3 |
| $S_{\lambda+\text{bg}}$ | 1.52 | 1.52 | 1.60 |
| S_{bg} | 0.07 | 0.06 | 0.08 |

The calibration graph was plotted from the following points:

| | | | | | |
|----------------------|------|-------|-------|-------|-------|
| $\log C$ | -5.0 | -4.52 | -4.00 | -3.52 | -3.00 |
| $\log I_{\text{an}}$ | 0.38 | 0.70 | 1.11 | 1.61 | 1.98 |

The data to be used for plotting the characteristic curve of the photographic plate with the spectra of the sample are as follows:

| | | | | | | | | | |
|-----|------|------|------|------|------|------|-------|-------|-------|
| S | 0.02 | 0.04 | 0.10 | 0.21 | 0.30 | 0.73 | 1.02 | 1.40 | 1.70 |
| I | 0.35 | 0.52 | 0.82 | 1.25 | 1.80 | 5.00 | 10.00 | 20.00 | 42.00 |

25. To determine the content of tin in an ore use was made of a procedure of emission spectroscopic analysis with photo-

graphic recording, according to which the calibration graph is to be plotted by the "three-standard method" and the unknown sample and standards are burned three times. At concentrations of 10^{-3} to 10^{-2} per cent the coefficient of variation of the procedure used is ± 9 per cent.

The sample was split up into three parts which were analysed in different days. The results of the determination are presented in Table 29.

TABLE 29

| Sample | Percentage of tin | $\Delta S_{\text{an, av}}$ | | |
|------------|-------------------|----------------------------|---------|---------|
| | | plate 1 | plate 2 | plate 3 |
| Standard 1 | $1 \cdot 10^{-3}$ | —0.05 | —0.09 | 0.00 |
| | — | —0.03 | —0.11 | —0.05 |
| | — | —0.07 | —0.08 | —0.06 |
| 2 | $3 \cdot 10^{-3}$ | +0.22 | +0.23 | +0.19 |
| | — | +0.23 | +0.23 | +0.17 |
| | — | +0.25 | +0.27 | +0.21 |
| 3 | $1 \cdot 10^{-2}$ | +0.56 | +0.60 | +0.57 |
| | — | +0.64 | +0.62 | +0.56 |
| | — | +0.53 | +0.65 | +0.55 |
| 4 | $3 \cdot 10^{-2}$ | +0.97 | +0.93 | +0.85 |
| | — | +0.92 | +0.90 | +0.82 |
| | — | +0.92 | +0.88 | +0.88 |
| Unknown | C | +0.39 | +0.40 | +0.42 |
| | — | +0.39 | +0.43 | +0.35 |
| | — | +0.38 | +0.38 | +0.34 |

Determine the percentage content of tin in the sample from the results of the measurements.

26**. A quantometer was calibrated with the aid of four standards and the following readings of the instrument, averaged over a number of measurements, were obtained:

| | | | | |
|-------------------------------|------|------|------|-----|
| Standard | 1 | 2 | 3 | 4 |
| Percentage of Cr | 0.17 | 0.41 | 0.91 | 2.0 |
| Quantometer reading | 46 | 32 | 19 | 8 |

The instrument readings were checked every shift with the aid of standard 2, for which purpose three successive measurements were made. The averaged values of readings

used for checking were as follows: 32, 32.1, 31.9, 31.8, 31.9, 32.0, 32.1, 32.2, 32.1, 32.3, 32.2, 32.3, 32.4, 32.3.

Find out when the calibration of the instrument began shifting if the coefficient of variation of the analytical

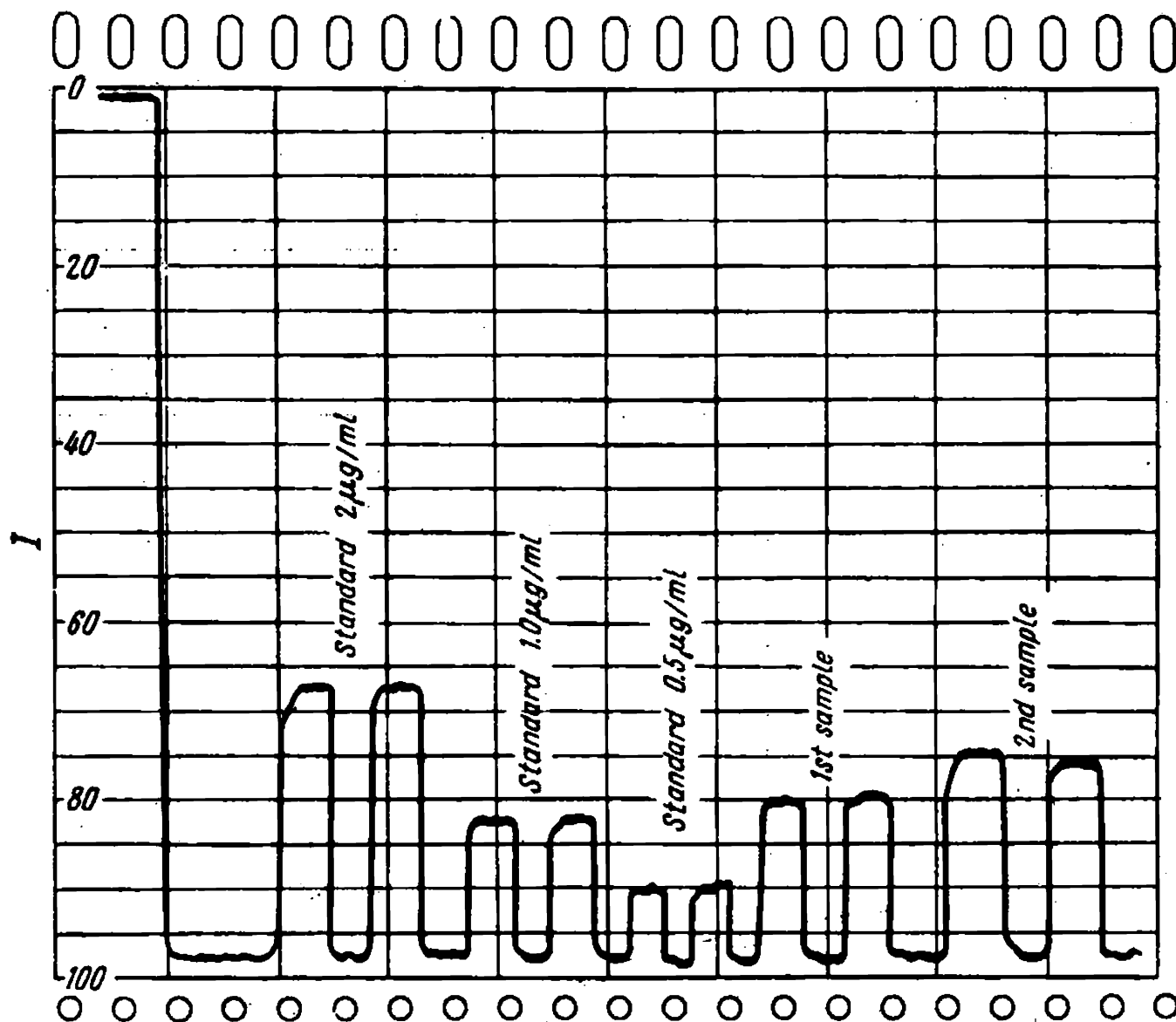


Figure 43

method in taking the readings once is ± 1.2 per cent for a concentration of chromium of 0.3 to 0.7 per cent.

27. In determining the content of copper in an ore use was made of the atomic-absorption method of analysis. A sample of ore weighing 1 g was dissolved in aqua regia and the resulting solution diluted with water to 100 cm³.

Determine the copper content in two samples of the ore from the record of the intensity of the 324.7 nm analytical copper line (see Fig. 43); the standard deviation of the method $\sigma = \pm 0.02$ $\mu\text{g/ml}$.

28. The composition of brass was analysed in the course of melting in an express laboratory with the aid of a quantometer. The spectra were excited in a d-c arc. The exposure time of the order of 30 sec was specified from the time of

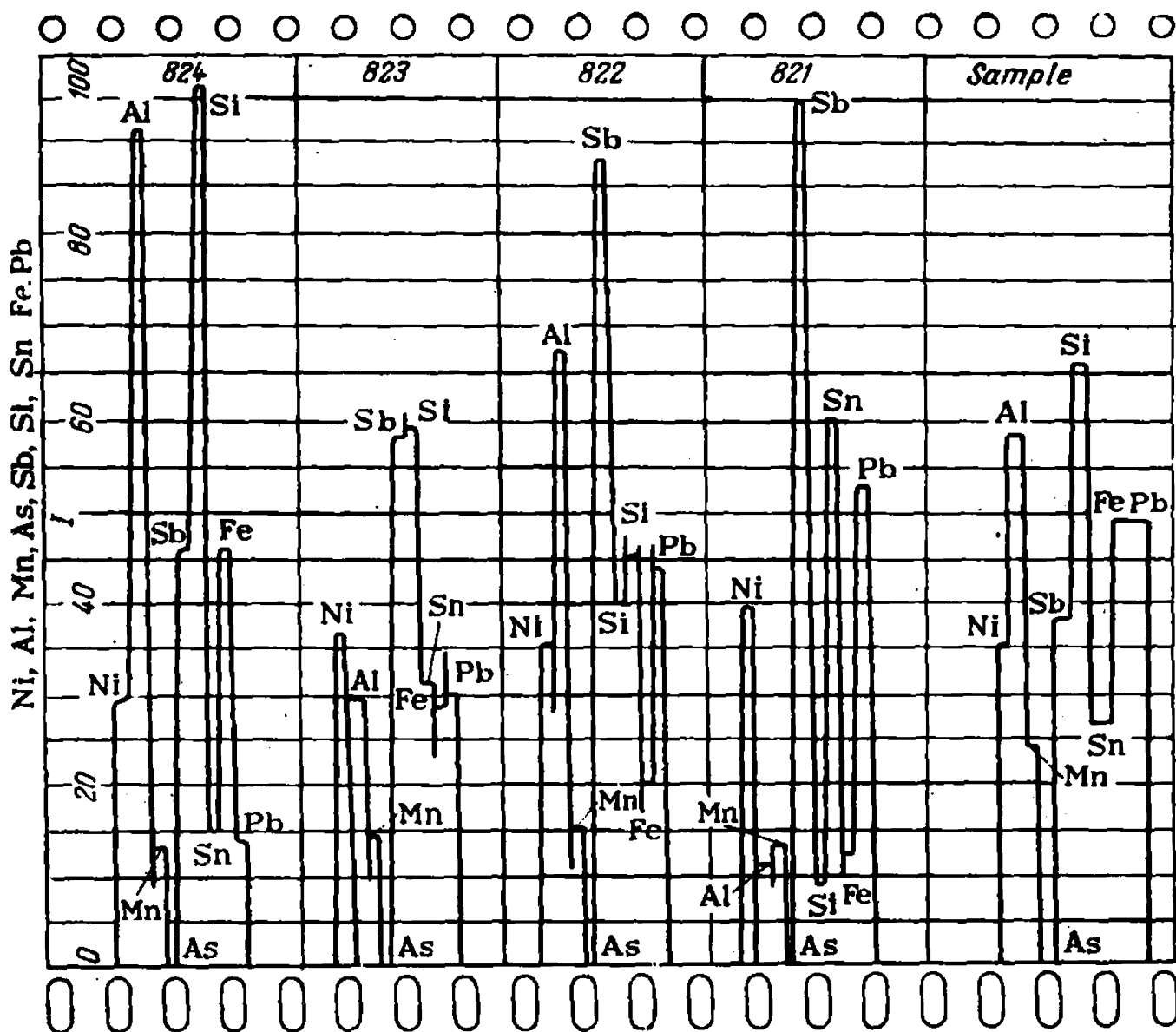


Figure 44

accumulation of electric charge on the condenser in the channel of the comparison line which was the copper spectrum line for all the elements. The trace record showing the results of the successive measurements of the relative line intensities of all the impurities being determined is given in Fig. 44. The composition of the standards is indicated in Table 30.

Plot a calibration graph from the spectra of the standards, assuming that the magnitude of the photoelectric signal

TABLE 30

| Standard sample | Composition, per cent | | | | | | |
|-----------------|-----------------------|------|------|-------|------|-------|-------|
| | Pb | Fe | Ni | Si | Sn | Al | Sb |
| 824 | 0.73 | 0.43 | 0.49 | 0.58 | 0.12 | 0.54 | 0.005 |
| 823 | 1.08 | 0.29 | 0.68 | 0.30 | 0.22 | 0.15 | 0.010 |
| 822 | 1.42 | 0.20 | — | 0.19 | 0.30 | 0.32 | 0.016 |
| 821 | 1.82 | 0.16 | 0.88 | 0.059 | 0.43 | 0.073 | 0.019 |

measured from the trace record (in mm) is proportional to the relative intensity of the analytical line. Determine the contents of lead, iron, nickel, silicon, tin, aluminium, and antimony in the sample.

29. In working out a procedure of X-ray spectroscopy for analysis of copper-based alloys it was found that the instrument readings for the copper line depend on the concentration of lead in the samples:

| | | | | | | | | |
|--|------|------|------|------|------|------|------|------|
| C_{Cu} , % | 54.1 | 54.2 | 57.8 | 61.5 | 61.7 | 62.7 | 64.5 | 64.6 |
| C_{Pb} , % | 3 | 1 | 2 | 2 | 3 | 1 | 2 | 1 |
| Instrument reading (counts/min) · 10 ³ | 805 | 820 | 866 | 920 | 915 | 945 | 964 | 972 |

What is the maximum error of the analysis due to the effect of the alloy composition if the instrument has been calibrated for determination of the copper content by using standards containing 2 per cent of lead and the possible range of variation of the concentration of this element in the samples is 1.5 to 2.5 and 1 to 3 per cent?

Compare these errors with the statistical error due to the discrete nature of radiation.

30**. The laboratory has received an unmarked brass article for analysis. To determine the brass grade without damaging the article, the spectrum of the metal was recorded with the aid of an X-ray spectrum scanning analyser having a quartz crystal with reflecting (1010) planes.

Determine the brass grade, using the schematic representation of the spectrum in Fig. 45.

31*. For a qualitative analysis of a polymetallic ore, a portion of the X-ray spectrum of the unknown sample and

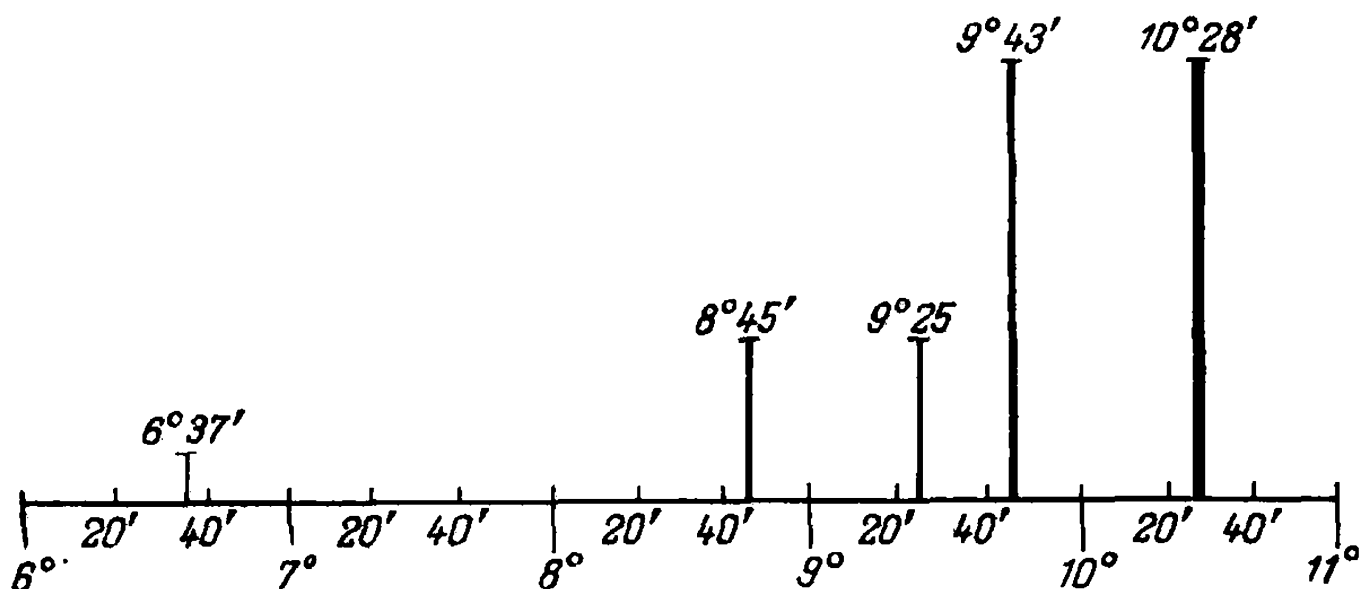


Figure 45

the spectrum of pure iron (see Fig. 46) were photographed on film. The spectral range of the instrument is 0.05 to 0.2 nm. The voltage on the X-ray tube is 50 kV.

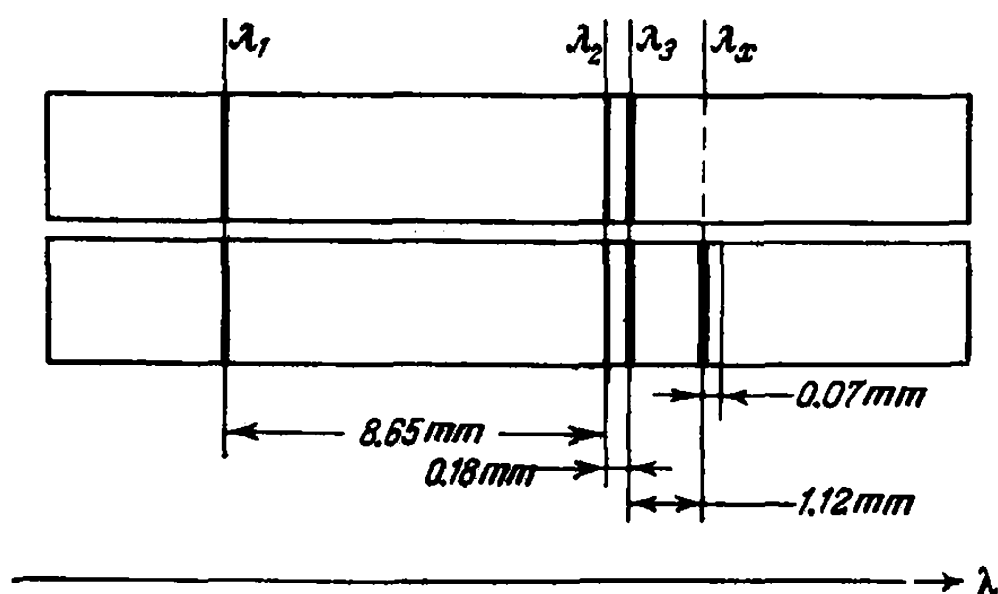


Figure 46

Identify the unknown line λ_x , assuming the dispersion of the analyser to be constant over the entire portion of the spectrum being examined.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. Why are several dispersing prisms to be used in spectral instruments?

(a) To increase the illuminating power (speed) of the instrument.

(b) To widen the spectral range of the instrument.

(c) Such instruments are easy to construct because they do not require increased accuracy of design.

(d) To increase the angular dispersion of the instrument.

(e) To reduce the speed of the instrument.

2. Which of the following lines are used in the homologous-pair method?

(a) Closely spaced lines of an element, differing in intensity.

(b) The lines of the unknown element and the standard, whose intensity does not vary with change of excitation conditions.

(c) The lines of the unknown element and the standard, whose intensity ratio does not vary with change of excitation and vaporization conditions.

(d) The lines of the unknown element and the standard, whose intensities change differently with change of excitation conditions.

(e) Closely spaced lines of the element being determined, whose intensity ratio determines the concentration of the element.

3. Figure 47 shows a block diagram of an instrument used for fluorescent X-ray spectral analysis. Which of the answers given below indicates the correct layout of the instrument.

| | 1 | 2 | 3 | 4 | 5 |
|-----|---------------------------|----------|-------------------------------|-------------------|-------------------------------------|
| (a) | Source of X-ray radiation | Sample | Receptor of X-ray spectrum | Spectrum recorder | Device for measuring line intensity |
| (b) | Source | Receptor | Device for amplifying signals | Recorder | Device for measuring line intensity |

| | | | | | |
|-----|--------|-------------------------------|-------------------------------|--|--|
| (c) | Source | Device for amplifying signals | Receptor | Device for measuring line intensity | Device for recording results of analysis |
| (d) | Source | Receptor | Sample | Instrument for amplifying line intensity of spectrum | Recorder of spectrum line intensity |
| (e) | Source | Sample | Device for amplifying signals | Receptor | Device for measuring line intensity |



Figure 47

4. When measuring the line intensity of chromium and the background in the spectra of an unknown substance and the standard the following data were obtained (the intensity was measured in arbitrary units):

| Sample Photocurrent | Unknown | Standard I (chromium, 1.5%) | Standard II (chromium, 2.8%) |
|------------------------|---------|-----------------------------------|------------------------------------|
| i_s | 20 | 15 | 32 |
| i_{bg} | 2 | 3 | 2 |

Which of the formulas given below can be used to calculate the content of chromium in the unknown if there is a linear relationship between the quantities used for calculations.

(a) $C_x = 1.5 + \frac{2.8 - 1.5}{32 - 15} (20 - 15) = 1.88 \text{ per cent.}$

$$(b) C_x = 2.8 - \frac{\log 2.8 - \log 1.5}{\log \frac{32}{2} - \log \frac{15}{3}} \left(\log \frac{20}{2} - \log \frac{15}{3} \right) =$$

$$= 1.9 \text{ per cent.}$$

$$(c) C_x = 2.8 + \frac{\log 2.8 - \log 1.5}{\log 32 - \log 15} (\log 20 - \log 15) =$$

$$= 2.99 \text{ per cent.}$$

$$(d) C_x = 1.5 - \frac{\log 2.8/1.5}{\log 32/15} \log 20/15 = 1.40 \text{ per cent.}$$

(e) The unknown concentration cannot be calculated from the data given.

5. Which of the instruments listed below can be used as a receptor (detector) of X-ray radiation in ordinary analytical apparatus?

- (a) Geiger-Müller counter.
 - (b) Photographic plates for the visible region of the spectrum.
 - (c) Photomultipliers.
 - (d) Scintillation counters.
 - (e) Proportional photon counters.
 - (f) Photocells.
 - (g) Thermoelements.
 - (h) Photocells for the ultraviolet region of the spectrum.
6. For what purposes is a step attenuator used in spectral analysis?

- (a) To decrease the brightness of lines that interfere with the determination.
- (b) To increase the sensitivity of the determination.
- (c) To plot the characteristic curves of photographic plates.
- (d) To intensify weak spectroscopic lines.
- (e) To weaken the fog of the plate.
- (f) For photoelectric measurement of line intensity.
- (g) In express determination of the intensity ratio of the lines being compared.
- (h) To widen the region of normal blackening.

7. Figure 48 shows the curves for the burning of 3 unknown elements, A, B and C, and of the parent metal P (a multi-line component). Which of the following answers reflects the conditions of determination of these elements if the wave-

lengths at which the determinations are made and the wavelengths of the base are unresolvable (because they are close to one another).

(a) All the three elements can be determined without preliminary burning in the following intervals of spectrum

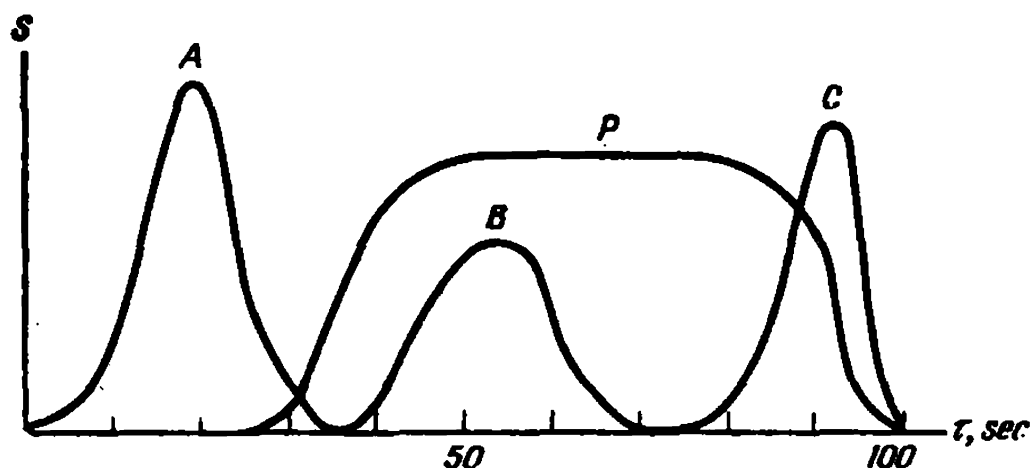


Figure 48.

photographing: 0-35 sec for A, 35-70 sec for B, and 70-100 sec for C.

(b) The substance A can be determined without preliminary burning, the spectrum being recorded within an interval of 0 to 30 sec.

(c) When the preliminary burning takes 100 sec, the spectrum of B can be recorded in a time interval of 100 to 130 sec.

(d) Neither of the elements indicated can be determined.

(e) The determination of B and C is impeded by the vaporization of the principal constituent.

(f) The vaporization of the principal component interferes with the determination of A and B, whereas C can be determined after the preliminary burning (60 sec) and the photographing of the spectrum (60 to 100 sec).

(g) The vaporization of the principal constituent interferes with the determination of A and does not interfere with the determination of B and C.

(h) The principal component can be removed by burning the sample for 100 sec. Then the components A, B, and C are determined successively at the following exposure times, respectively: 0 to 35 sec, 35 to 65 sec, and 65 to 100 sec.

8. Find under B the optical characteristics of the dispersing elements given under A.

A

- (a) Quartz prism.
- (b) Iceland spar prism.
- (c) Planar diffraction grating.
- (d) Prism made of calcium fluoride.
- (e) Concave diffraction grating.
- (f) Glass prism.
- (g) Prism with one reflecting surface.
- (h) Metallic mirrors.

B

(1) This dispersing element not only resolves radiation into a spectrum but also focuses beams of monochromatic light.

(2) This dispersing element is used in spectroscopes for the visible region of the spectrum.

(3) Instruments equipped with this dispersing element enable the ultraviolet, visible, and infrared regions of the spectrum to be observed.

(4) This dispersing element is used in instruments for studying the ultraviolet and visible regions of the spectrum.

(5) The angular dispersion of this dispersing medium is independent of the wavelength. Extra lenses or mirrors are required for monochromatic beams to be focused.

(6) In this dispersing element, one surface is covered with a coat of silver and the light ray traverses the prism twice, in opposite directions. The use of this type of prism enables the design of the spectral instrument to be simplified.

(7) This dispersing element is used only in instruments for photographing infrared spectra.

(8) This dispersing element is used only for observations in the ultraviolet region of the spectrum.

(9) This dispersing element is used in instruments for X-ray analysis.

(10) Not used as a dispersing device.

9. Find under B the definition and under C the equation that could be used to calculate the quantities under A characterizing spectral instruments.

A

- (a) Linear dispersion.
- (b) Angular dispersion.
- (c) Resolving power.
- (d) Speed (luminosity).
- (e) Spectral range.

B

(1) This is the magnitude of the angle by which light rays whose wavelength difference is 0.1 nm will diverge in the camera part of the instrument.

(2) This quantity is measured by the ratio of the square of the camera lens diameter to its focal length.

(3) This quantity is measured by the ratio of the distance between two closely spaced lines in millimetres to the difference in the lengths of these lines in nm.

(4) This quantity is measured by the interval of the wavelengths recorded by the instrument.

(5) This quantity is measured by the ratio of the mean of two neighbouring wavelengths that are separated by the instrument to their difference.

C

(1) $\frac{\lambda}{\Delta\lambda}$.

(2) $\lambda_{\max} - \lambda_{\min}$.

(3) $D = \frac{\Delta L}{F_{\text{cam}}}$.

(4) $L = \left(\frac{D_{\text{cam}}}{F_{\text{cam}}} \right)^2$.

(5) $D = \frac{\Delta L}{\Delta\lambda}$.

10. Indicate under A the function performed by a buffer in spectral analysis, and under B the substances that are most often used as the buffer.

A

(a) Buffers are used to increase the melting temperature of the sample.

(b) Buffers are introduced into the sample to obtain spectral lines with which the line intensity of the elements being determined could be compared.

(c) Buffers enable one to obtain the most favourable ratio of the rates of vaporization of the components of the sample.

(d) Buffers serve only for the purpose of diluting the sample.

(e) Buffers serve to reduce the intensity of spectral lines by decreasing the concentration of the unknown elements.

B

(1) High-melting metallic powders.

(2) Powdered carbon, pure or containing substances capable of forming compounds of required volatility with the unknown components.

(3) Powdered quartz.

(4) Powdered quartz, to which are added substances forming with the unknown components high-melting and low-volatile compounds.

(5) A mixture of powdered carbon and quartz.

Electrolysis and Coulometric Analysis

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. How much oxygen (in grams) and hydrogen (in litres) will be evolved during the electrolysis of sulphuric acid for 15 minutes if the current is 2.5 A?

Solution: The quantity of electricity passed through the solution is equal to

$$Q = i\tau = 2.5 \times 0.25 = 0.625 \text{ A} \cdot \text{hr}$$

The passage of 26.8 A·hr results in the evolution of one gram-equivalent of oxygen, i.e., 8 g, and when 0.625 A·hr is passed the amount of oxygen evolved is

$$\frac{0.625 \times 8}{26.8} = 0.186 \text{ g}$$

The passage of 26.8 A·hr results in the evolution of 1 g-eq of hydrogen, which occupies a volume of 11.2 litres; hence, when 0.625 A·hr is passed the amount of hydrogen evolved will be

$$\frac{0.625 \times 11.2}{26.8} = 0.26 \text{ litre}$$

Example 2. In a coulometric determination of zinc 35.4 ml of a mixture of hydrogen and oxygen was evolved during the complete reduction of zinc in a gas coulometer.

Determine the zinc content in the solution.

Solution: The electrolysis of one mole of water results in the formation of 22.4 litres of hydrogen and 11.2 litres of oxygen. The total volume, 33.6 litres, corresponds to 1 g-eq of zinc; which is equal to $65.4/2 = 32.7$ g. We set up the proportion:

$$\begin{array}{r} 33.6 - 32.7 \\ 0.0354 - x \\ x = \frac{0.0354 \times 32.7}{33.6} = 0.0342 \text{ g} \end{array}$$

Example 3. On coulometric titration of 20 ml of potassium dichromate with electrolytically generated iron(II) it took 25 min to reduce $\text{Cr}_2\text{O}_7^{2-}$ at a current of 200 mA.

Determine the normality of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution being analysed.

Solution: The quantity of electricity passed through the solution is $Q = i\tau = 25 \times 60 \times 0.200 = 300$ C. The passage of 96,500 coulombs reduces 1 g-eq of $\text{K}_2\text{Cr}_2\text{O}_7$. The passage of 300 coulombs results in the evolution of $300/96,500 = 0.0032$ g-eq.

Twenty millilitres of the solution contain 0.0032 g-eq and, hence, the normality of the solution being analysed is

$$\frac{0.0032}{20} \times 1000 = 0.160$$

2. MULTIVARIANT PROBLEMS

1. Using the data given, determine the parameter designated by x (see Table 31).

TABLE 31

| Variant | Substance or ion | Current, A | Electrochemical equivalent | Time, min | Amount of substance evolved |
|---------|-----------------------------|------------|----------------------------|-----------|-----------------------------|
| I | — | 2.5 | 1.97 g/(A·hr) | 4 | x |
| II | Trivalent metal ion | 3 | x | 3.5 | 0.2752 g |
| III | Bivalent metal ion | 1.8 | 0.3054 mg/C | 1.42 | x mg |
| IV | Silver salt | 2.5 | 4.025 g/A·hr | x | 0.5450 g |
| V | Molten KCl | x | 0.368 | 1.5 | 0.25 litre of Cl_2 |
| VI | Trivalent metal ion | 15 | 0.093 mg/C | x | 3.78 g |
| VII | Solution of CdCl_2 | x | — | 25 | 0.300 g |
| VIII | Univalent metal ion | 0.35 | x mg/C | 2.35 | 0.1037 g |

2. Calculate the amount of substance that has reacted in a coulometric separation at constant potential from the data given in Table 32.

TABLE 32

| Variant | Process | Amount of substance evolved in coulometer |
|---------|---|--|
| I | $\text{Cu}^{2+} \rightarrow \text{Cu}^0$ | 34.5 ml of hydrogen |
| II | $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ | The titration of the iodine evolved in the coulometer required 10.5 ml of a 0.15N solution of thiosulphate |
| III | $\text{Ti}^{3+} \rightarrow \text{Ti}^{\text{IV}}$ | 35 ml of a mixture of hydrogen and oxygen |
| IV | $[\text{Fe}(\text{CN})_6]^{4-} \rightarrow [\text{Fe}(\text{CN})_6]^{3-}$ | The difference in the masses of copper electrodes is 0.0125 g |
| V | $\text{H}^+ \rightarrow \text{H}_2$ | The concentration of potassium iodide decreased from 2 to 0.5N |
| VI | $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$ | 314 ml of gas having a density of 17.75 with respect to helium |
| VII | $\text{Mn}^{2+} \rightarrow \text{MnO}_4^-$ Determine the normality of the solution obtained with respect to $\text{H}_2\text{C}_2\text{O}_4$. The volume is 100 ml | 0.250 litre of H_2 |
| VIII | $\text{H}^+ \rightarrow \text{H}_2$ Determine the variation of the concentration of 1N solution. The volume is 200 ml | 0.1560 g was deposited on the cathode of a silver coulometer |

3. Determine the content of the ion indicated (in mg) by the method of coulometric titration at constant current:

TABLE 33

| Variant | Ion or substance being determined | Ion or substance generated | Current, mA | Time, min |
|---------|-----------------------------------|--------------------------------------|-------------|-----------|
| I | Fe^{2+} | Br_2 | 100 | 3.5 |
| II | H^+ | OH^- | 300 | 5 |
| III | Se^{IV} | I^- | 200 | 7 |
| IV | Mo^{V} | Fe^{2+} | 150 | 15 |
| V | BO_3^{3-} | OH^- | 100 | 10 |
| VI | Pyridine | H^+ | 120 | 5.5 |
| VII | Theobromine | I^- | 250 | 3 |
| VIII | Zn^{2+} | $\text{K}_3[\text{Fe}(\text{CN})_6]$ | 300 | 4.1 |

3. PROBLEMS

SECTION A

1. Determine the time required for 0.1 g of iron to be deposited in the electrolysis of a solution of FeCl_3 if the current is 4 A. How much chlorine (in ml) will be deposited at the anode?

2. A current of 2.5 A is passed through several electrolytes during 40 min. How many grams and millilitres and of what substances will be deposited on the anode and cathode in the electrolysis of solutions of H_2SO_4 , CuSO_4 , CoCl_2 , KOH , $[\text{Ag}(\text{NH}_3)_2]\text{OH}$, $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$?

3. Calculate the amount of a trivalent metal with an electrochemical equivalent of 0.5430 mg/C deposited on electrolysis for 1 min 25 sec if the current is 1.8 A. What metal is it?

4. At a constant current of 0.19 A it took 50 min to deposit copper on the cathode and lead as PbO_2 on the anode from an alloy sample weighing 1.835 g.

Find the gain in the weight of the anode and cathode and the content of lead and copper in the sample (in per cent).

5. A platinum cathode and a silver anode are dipped into a vessel containing 500 ml of water acidified with nitric acid.

How long does it take to produce a solution of silver nitrate having a titre of 0.002 g/ml with respect to the thiocyanate ion in the electrolytic dissolution of the anode at a current of 1.5 A?

6. The complete electrolytic deposition of zinc from 2.250 g of zinc ore after appropriate treatment required 18.5 min at a current of 1.15 A.

Determine the quantity of deposited zinc and the percentage content of zinc in the ore.

7. What amount of a cyanide complex of copper is required to cover a surface area of 300 cm^2 with a layer of copper of 0.5 mm and how long will the electrolysis proceed at a current of 5 A?

8. In a coulometric determination of picric acid, $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_3$, 11.5 ml of a 0.01N solution of sodium thiosulphate was needed to titrate the iodine evolved in the coulometer.

Determine the content of picric acid in the solution if 18 electrons participate in its reduction.

9. Hydrochloric acid is titrated coulometrically with electrolytically generated ions OH^- at a constant current of 10 mA. The point of equivalence on titration of 5 ml of the solution being analysed is reached for 3 min 10 sec.

Calculate the titre of the HCl solution with respect to NaOH.

SECTION B

10. A silver salt solution deposits silver completely on electrolysis during 30 min if the current is 3 A.

What current is required for the initial concentration of the solution to decrease by a factor of two for 10 min?

11. Calculate the electrochemical equivalent of a trivalent metal if the electrolysis of a solution of its salt at a current of 3 A deposits 0.5815 g of the metal for 35 min. What metal is it?

12. To produce a cadmium amalgam by electrolysis a current of 0.5 A was passed through a solution of a cadmium salt for 4 min.

Calculate the percentage content of cadmium in the amalgam if the cathode used for its preparation consisted of 15 g of mercury.

13. A sample of copper sulphate weighing 58.4 g and containing 7 per cent of impurities was dissolved in 500 ml of water.

How much of this solution must be added to the galvanic cell to compensate for the amount of copper used up if the electrolysis was carried out for 3 hours at a current of 1.5 A?

14. The copper containing bismuth as an impurity is deposited electrolytically from a 1M solution of copper sulphate.

Calculate the amount of copper that must be left in the solution in order to prevent the codeposition of bismuth.

15. In the coulometric titration of hydrochloric acid, a solution of K_2SO_4 was electrolysed with a current of 3 mA. On addition of 50, 60, 80, and 100 drops of hydrochloric acid the electrolysis took, respectively, 140, 180, 250, and 300 sec.

Calculate the mean value of the normality of the hydrochloric acid and the error of determination of S if the volume of one drop is 0.025 ml.

16. In a coulometric determination of cobalt in 1.5 g of a metal in a silver coulometer, 0.0755 g of silver was deposited.

Determine the percentage content of cobalt in the metal.

How long will it take to deposit electrolytically 0.80 g of cobalt from the solution at a current of 250 mA?

SECTION B

17. In the coulometric titration of KMnO_4 with electrolytically generated ions Fe^{2+} at constant potential the initial current, 150 mA, decreased linearly with time and dropped down to zero after 120 sec.

Calculate the concentration of KMnO_4 if 3.5 ml of this solution was taken for titration.

18. In a coulometric investigation of the reduction of a complex, the weight increase of the copper electrode in the coulometer was 0.0012 g. The amount of the reduced complex was 0.0183 g. Its molecular weight is 1788 g.

Determine the number of electrons taking part in the reduction.

19. For a coulometric determination of furan in tetrahydrofuran two samples of tetrahydrofuran weighing 0.05 g each are simultaneously titrated with electrolytically generated bromine under the following conditions:

| | 1st sample | | | 2nd sample | | |
|----------------------------------|------------|-----|------|------------|------|------|
| Current, mA | 10 | 13 | 18 | 25 | 35 | 40 |
| Time of titration, sec | 168 | 126 | 91.5 | 115 | 83.5 | 70.5 |

The time required to titrate the original tetrahydrofuran is 15 sec at a current of 5 mA (due to the presence in it of the impurities liable to bromination).

Determine the content of furan in the mixture of these samples (3 : 2).

20**. In a coulometric analysis of a solution containing cadmium and zinc there was deposited 0.405 g of the metals during the electrolysis time. During the same time 0.2750 g of silver was deposited in the silver coulometer.

Determine the content of cadmium and zinc in the solution (in grams).

21. When nickel was electrolytically deposited from a solution of 1 g of an alloy containing 9.63 per cent of nickel for 360 min at a current of 1.5 A, the deposited metal was found to contain cobalt as an impurity.

Determine the percentage content of cobalt in the alloy, assuming that the current is distributed proportionately to the content of the metals.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. Which of the following answers reflects most fully the factors that govern the potential of a metal electrode in a solution of its salt (*a* — according to the Nernst formula, and *b*—additional factors affecting the potential)?

- (1) *a*—Temperature, pressure, ion concentration.
b—The ionic strength of the solution.
- (2) *a*—Temperature, ionic activity.
b—Hydrogen ions, extraneous substances, the condition of the electrode surface.
- (3) *a*—Ionic activity.
b—Temperature, hydrogen ion concentration.
- (4) *a*—Ionic activity, temperature, ligand concentration.
b—The condition of the electrode surface.
- (5) *a*—Temperature, the ionic strength of the solution, ion concentration.
b—Other factors do not affect the potential.

2. Why must the evolution of hydrogen be avoided during the electrolytic deposition of a metal from acidic solutions?

(a) If hydrogen is evolved at the electrode, the metal will not be deposited.

(b) The simultaneous hydrogen evolution and metal deposition at the electrode leads to the formation of high-melting and difficultly soluble hydrides, and the deposit is very difficult to remove from the electrode.

(c) The simultaneous hydrogen evolution and metal deposition results in the reduction of metal oxides and in the decrease of the metal weight.

(d) The codeposition of hydrogen results in the metal being saturated with hydrogen and in the formation of loose spongy deposits.

(e) The evolution of hydrogen does not interfere with the electrolytic deposition of metals.

3. Under what conditions in electrolysis could there be obtained strong metal deposits?

(a) When the electrolysis is carried out at more positive potentials than the potentials of hydrogen evolution and deposition of other metals present with account taken of their overpotentials. Electrolysis should be carried out at mean current densities, preferably in the presence of ligands.

(b) When electrolysis is carried out from acidic solutions at more positive potentials than the potential of hydrogen evolution, at low temperatures and high current densities.

(c) The solution should be strongly acidified and the electrolysis carried out at mean current densities under the conditions of hydrogen codeposition.

(d) In carrying out the electrolysis it is necessary to remove hydrogen ions and all the extraneous metal ions present from the solution. The electrolysis should be conducted at the boiling temperature in the presence of ligands that form the most stable complexes with the metal ion being determined.

(e) The electrolysis should be carried out exactly at the metal deposition potential in the presence of complex-forming substances; the hydrogen ions present should be preliminarily removed electrolytically from the solution.

4. Can coulometric titration be carried out at constant potential?

(a) Yes, without any additional limitations.

(b) Yes, but the potential must be kept constant with an accuracy of thousandths of a volt.

(c) Yes, but it is necessary to determine, in the course of titration, the quantity of electricity consumed until the equivalence point is reached. The determination is made graphically in the coordinates of current vs. time or with the aid of a coulometer.

(d) Yes, but the titration must be carried out at currents of the order of several microamperes.

(e) Coulometric titration cannot be conducted at constant potential.

5. Which of the following formulas should be used to calculate the emf of the cell



if the standard redox potential of $\text{Cu}^{2+}/\text{Cu}^0$ is equal to $+0.34$ V?

(a) $E = 0.34 + 0.058 \log 1/0.1 = 0.398$ V.

(b) $E = 0.058/2 \times \log 1/0.1 = 0.029$ V.

(c) $E = 0.34 + 0.058/2 \times \log 0.1/1 = 0.311$ V.

(d) $E = 0.058 \log 1/0.1 = 0.058$ V.

(e) The data given are insufficient for calculation.

6. Which of the following formulas could be used to determine the amount of hydrogen (in ml) that would be evolved during the electrolysis at a current of 0.2 A for 5 minutes?

(a) $V = \frac{0.2 \times 5 \times 22,400}{96,500} = 0.23$ ml.

(b) $V = \frac{0.2 \times 5 \times 60 \times 22,400}{96,500} = 13.8$ ml.

(c) $V = \frac{0.2 \times 5 \times 60 \times 22.4}{26.8} = 50.2$ ml.

(d) $V = \frac{0.2 \times 5 \times 2}{26.8} = 0.75$ ml.

(e) $V = \frac{0.2 \times 5 \times 60 \times 22,400}{96,500 \times 2} = 6.9$ ml.

7. Which of the following answers characterizes correctly the process of electrode polarization?

(a) The electrode is polarized when it is immersed in a solution of a weak acid.

(b) The concentration polarization is associated with the electrochemical reactions taking place in the solution.

(c) The electrode becomes polarized when the ionization current is lower than the discharge current.

(d) The electrode becomes polarized when it is immersed in a solution of an extraneous salt.

(e) The concentration polarization arises when the amount of ions supplied to the electrode from the solution is lower than that being reduced at the electrode for the same time.

(f) The electrode becomes polarized as a result of the electrolytic evolution of hydrogen or oxygen at the electrode.

(g) The electrode dipped into any solution becomes polarized.

(h) At the state of equilibrium the logarithm of the exchange current is proportional to the potential and a deviation from the proportionality results in the electrode being polarized.

8. Figure 49 is a plot of the decomposition potential of chlorides of various metals against the concentration of

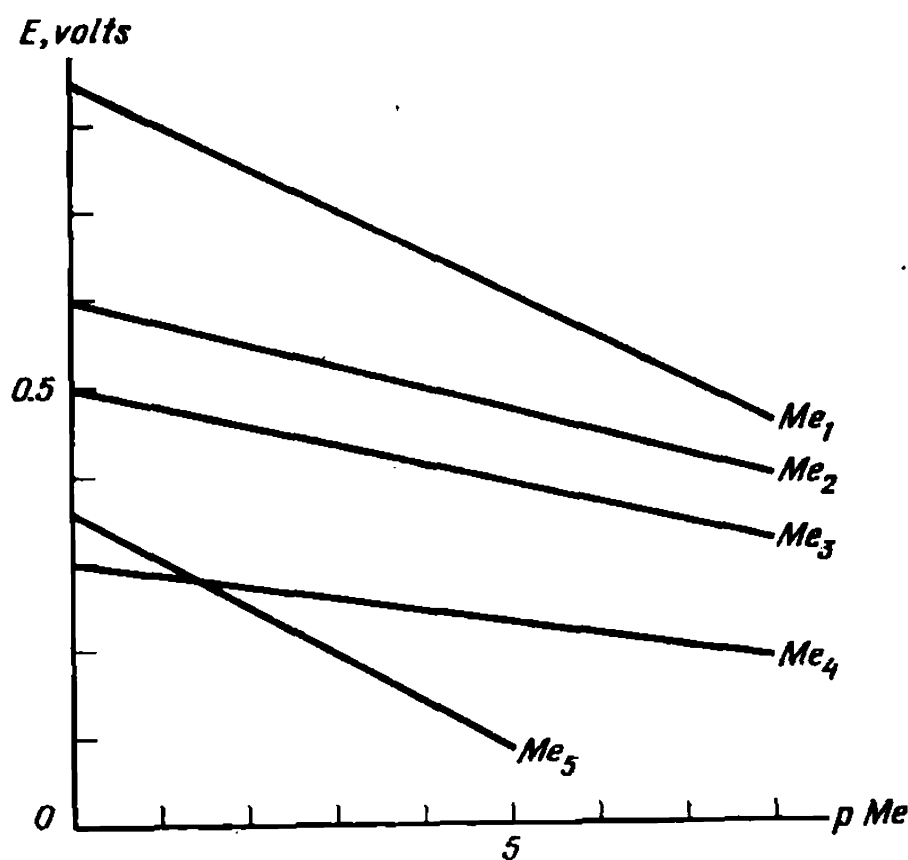


Figure 49

a metal in the solution. Which of the following answers characterizes correctly the possibility of separate deposition of these metals?

(a) When electrolysis is carried out at a potential of 0.35 V, the metal Me₃ can be separated from Me₄.

(b) The metals Me₂ and Me₃ will be deposited together at any potential.

(c) Me₂ can be separated electrolytically from Me₃, but not from Me₁.

(d) The metals Me₄ and Me₅ cannot be separated electrolytically.

(e) When electrolysis is carried out at a potential of 0.5 V, the metal Me_2 can be completely separated from Me_3 .

(f) The complete deposition of the metal Me_1 is impeded by Me_2 , but not by Me_3 or Me_4 .

(g) The metals Me_2 and Me_3 cannot be completely separated from each other by electrolysis.

(h) The metal Me_4 can be completely separated from Me_3 by electrolysis.

(i) When electrolysis is carried out at a potential of 0.35 to 0.30 V, the metal Me_5 can be completely separated from Me_4 .

(j) These metals cannot be separated electrolytically from one another.

9. The graphs in Fig. 50 show curves for the potential of hydrogen and the metals Me_1 and Me_2 versus the current density. Find the characteristics of the processes taking place as the current density increases.

(a) In this case, at any current density both metals will be deposited simultaneously with the evolution of hydrogen.

(b) Up to a current density of i_1 there will be deposited only Me_1 ; from i_1 to i_2 hydrogen will evolve simultaneously with the deposition of Me_1 , and at a current density higher than i_2 the evolution of hydrogen will predominate.

(c) The metal Me_2 will be deposited at a current density up

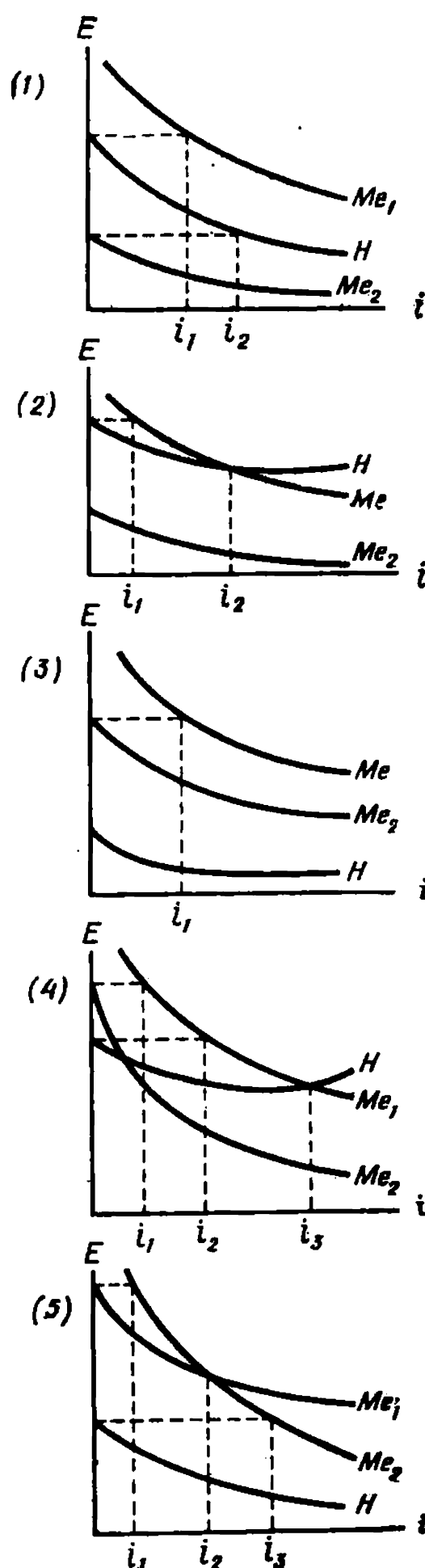


Figure 50.

to i_1 , and at a value higher than this Me_1 will be deposited simultaneously with the evolution of hydrogen.

(d) At a current density up to i_1 there will be deposited only Me_1 ; within the range between i_1 and i_2 the evolution of hydrogen begins, and beyond i_2 both metals are deposited simultaneously with the evolution of hydrogen.

(e) At a current density up to i_1 the metal Me_1 is deposited, in the region between i_1 and i_2 the metal Me_2 is deposited

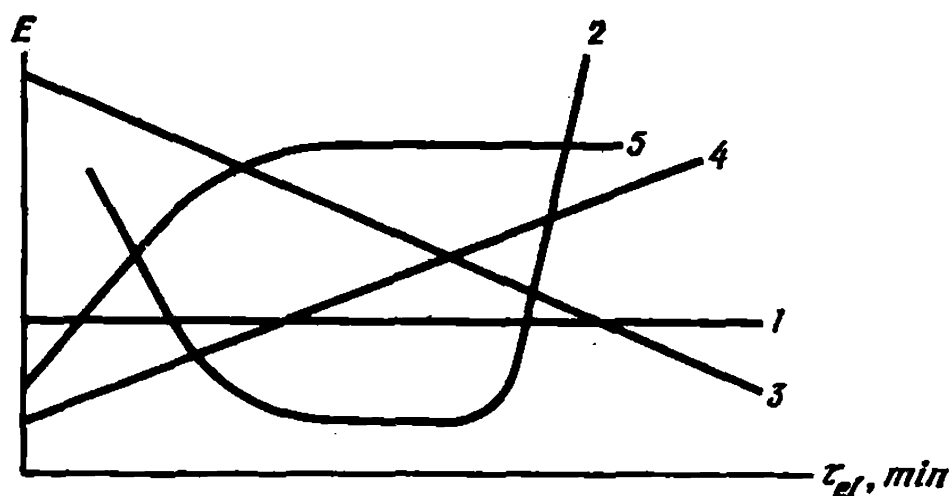


Figure 51

together with Me_1 and the evolution of hydrogen begins, and at a value higher than i_3 the evolution of hydrogen predominates.

(f) At a current density up to i_1 the metal Me_2 is deposited, within the range of i_1 to i_2 the deposition of Me_2 begins and hydrogen is evolved, and beyond i_3 the metal Me_1 begins to deposit.

(g) At a current density up to i_1 the metal Me_1 is deposited, and at a higher value the codeposition of Me_2 begins, the latter predominating.

(h) At a current density up to i_1 hydrogen is evolved, and between i_1 and i_2 the deposition of the two metals begins.

(i) At a current density up to i_1 the metal Me_2 is deposited, between i_1 and i_2 there is also deposited Me_1 , and at a current density higher than i_3 the evolution of hydrogen begins.

10. In Fig. 51 find the correct graph of the potential of the copper electrode against the electrolysis time. Indicate the correct explanation of this graph.

(a) Since in the course of electrolysis the electrode is covered with the metal, its surface area becomes larger and

the potential increases. After a certain period of time the concentration of copper ions begins to decrease and the potential is stabilized.

(b) Since in the course of electrolysis the concentration of copper ions is decreased, the electrode potential falls.

(c) Since during the electrolysis the temperature rises and the concentration of copper ions decreases, these processes compensate each other and the potential remains unchanged.

(d) Since the electrolysis involves complicated processes such as the increase of the electrode surface area, rise of temperature, and decrease of the concentration of copper ions, the electrode potential first falls and then begins to increase.

(e) Since during the electrolysis the concentration of copper ions decreases and the temperature rises, the electrode potential increases.

Conductometry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. The resistance of a 5 per cent solution of K_2SO_4 in an electrolytic cell, with the area of the electrodes being 2.54 cm^2 and the distance between them, 0.65 cm , equals 5.61 ohms . Find the equivalent conductance of the K_2SO_4 solution if the density of the solution may be assumed to be equal to unity.

Solution: We determine the electrical conductance of the solution:

$$W = \frac{1}{R} = \frac{1}{5.61} = 0.178 \text{ ohm}^{-1}$$

We determine the specific conductance (conductivity) of the solution:

$$W = \chi \frac{S}{L}; \quad \chi = \frac{WL}{S} = \frac{0.178 \times 0.65}{2.54} = 0.0458 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$$

We now calculate the number of gram-equivalents of K_2SO_4 in a unit volume (1 cm^3) of the solution being analysed:

$$n = \frac{5}{95 \times 87.13} = 6.039 \times 10^{-4} \text{ g-eq}$$

And, finally, we calculate the equivalent conductance:

$$\lambda = \frac{458 \times 10^{-4}}{6.039 \times 10^{-4}} = 75.8 \text{ ohm}^{-1} \cdot \text{g-eq}^{-1} \cdot \text{cm}^2$$

Example 2. The electrical conductivity of a $0.0109N$ solution of NH_4OH is equal to $1.02 \times 10^{-4} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

Determine the dissociation constant of NH_4OH .

Solution: We determine the equivalent conductance of the solution:

$$\lambda = \frac{1.02 \times 10^{-4} \times 1000}{0.0109} = 9.38 \text{ ohm}^{-1} \cdot \text{g-eq}^{-1} \cdot \text{cm}^2$$

The equivalent conductance at infinite dilution is calculated from table values of the mobilities of the ions NH_4^+ and OH^- :

$$\lambda_{\infty} = 76 + 205 = 281 \text{ ohm}^{-1} \cdot \text{g-eq}^{-1} \cdot \text{cm}^2$$

Now we calculate the degree of dissociation:

$$\alpha = \frac{9.38}{281} = 0.0334$$

Hence the dissociation constant is

$$K = \frac{\alpha^2 C}{1 - \alpha} = \frac{(0.0334)^2 \times 0.0109}{1 - 0.0334} = 1.26 \times 10^{-5}$$

2. MULTIVARIANT PROBLEMS

1. Using the data given in Table 35, draw a plot of conductance versus concentration. Determine the concentration in terms of the units indicated.

2. Using the data listed in Table 36, determine the parameter designated as x .

3*. At 18°C the specific resistance (resistivity) of water saturated with the difficultly soluble substances indicated in Table 34 is ρ_x .

TABLE 34

| Variant | Substance | $\rho \cdot 10^6$, ohm·cm | Variant | Substance | $\rho \cdot 10^6$, ohm·cm |
|---------|--------------------------|-------------------------------|---------|------------------|-------------------------------|
| I | SrC_2O_4 | 0.0185 | V | CaF_2 | 0.0217 |
| II | BaSO_4 | 0.417 | VI | TlCl | 0.00066 |
| III | PbSO_4 | 0.0307 | VII | TlCNS | 0.0009 |
| IV | CaC_2O_4 | 0.104 | VIII | AgBrO_3 | 0.0021 |

Determine the solubility and the solubility product if for water $\rho = 1.21 \times 10^6 \text{ ohm} \cdot \text{cm}$,

TABLE 35

| Var- ant | Substance | Concentration and electrical conductance | | | | | | Concentration being determined |
|-------------|--|--|--------|--------|--------|--------|--------|--|
| I | KOH in water | Normality | 0.05 | 0.1 | 0.2 | 0.3 | 0.5 | Grams per litre if con- ductivity is 0.058 ohm ⁻¹ .cm ⁻¹ |
| | | Equivalent conductan- ce, g-mole/cm ³ . . | 219 | 213 | 206 | 203 | 197 | |
| II | KNO ₃ in water | Normality | 0.01 | 0.05 | 0.1 | 0.5 | 1.0 | Grams per millilitre if resistivity is 45 ohms |
| | | Equivalent conductan- ce, g-mole/cm ³ . . | 118.2 | 109.9 | 104.8 | 89.2 | 80.5 | |
| III | NH ₄ Cl in water | Per cent by weight | 5 | 10 | 15 | 20 | 25 | Grams per litre if conductivity is 0.2250 ohm ⁻¹ .cm ⁻¹ |
| | | Conductivity, ohm ⁻¹ .cm ⁻¹ | 0.0918 | 0.1776 | 0.2586 | 0.3365 | 0.4025 | |
| IV | N ₂ H ₅ OH in water | Dilution | 1/16 | 1/32 | 1/64 | 1/128 | 1/256 | Normality if conduc- tivity is 0.041 ohm ⁻¹ .cm ⁻¹ |
| | | Molar conductance | 1.7 | 2.1 | 2.7 | 3.8 | 5.5 | |
| V | KI in alcohol | mg/25 ml | 0.52 | 1.04 | 1.78 | 2.41 | 3.35 | Normality if resistan- ce is 3.10 ohms |
| | | Resistance, ohms . . | 7.20 | 3.64 | 2.15 | 1.59 | 1.16 | |

| | | | | | | | | |
|------|----------------------------------|--|-------|-------|-------|-------|-------|---|
| VI | HCl in pyridine | Normality | 0.5 | 0.25 | 0.125 | 0.065 | 0.032 | Normality if resistance is 120 ohms |
| | | Resistance, ohms | 34.7 | 57.9 | 91.5 | 130 | 199 | |
| VII | CH ₃ COOH in water | Per cent by weight | 1 | 5 | 10 | 15 | 20 | Normality if resistance in a cell is 33.4 ohms and the cell constant is 28.6 ohms |
| | | Conductivity, ohm ⁻¹ .cm ⁻¹ | 3.50 | 1.46 | 0.90 | 0.64 | 0.47 | |
| VIII | Piperidine | 1 g in V litres. . . . | 0.107 | 0.214 | 0.428 | 0.856 | 1.712 | Molarity if conductivity is 1.67 × 10 ⁻³ ohm ⁻¹ .cm ⁻¹ |
| | | Conductivity × 10 ³ , ohm ⁻¹ .cm ⁻¹ | 2.88 | 2.05 | 1.38 | 0.925 | 0.608 | |

TABLE 36

| Vari- ant | Solution of sub- stance | Concentra- tion | Shape and size of electrode | Spacing of elect- rodes, cm | E, V | i, mA | R, ohms | Conductance | |
|--------------|---------------------------------|--------------------|-----------------------------------|--------------------------------------|------|-------|---------|-------------|-----------------|
| | | | | | | | | specific | equi- valent |
| I | AgNO ₃ | 1 mole/litre | Square, $l=1$ cm | 0.5 | — | — | x | — | 94.3 |
| II | AgNO ₃ | 0.05 mole/litre | Circle, $d=1.28$ cm | 1.68 | 0.5 | 5.96 | — | x | x |
| III | Na ₂ SO ₄ | — | $S=5.38$ cm ² | 0.82 | — | — | 2.86 | x | — |
| IV | H ₂ SO ₄ | 5 per cent | $S=3.8$ cm ² | 0.55 | 0.3 | x | — | 0.2 | — |
| V | CaCl ₂ | 10 per cent | Square, $l=1.5$ cm | 1.25 | x | 10 | — | 0.115 | — |
| VI | KCl | 1N, 20°C | Square, $l=x$ cm | 0.5 | — | — | 2.5 | — | — |
| VII | NaCl | 0.1N, 20°C | Circle, $d=1.5$ cm | x | 0.2 | 2.5 | — | — | — |
| VIII | HCl | — | $S=5.6$ cm ² | 1.8 | — | — | x | 0.2 | — |

3. PROBLEMS

SECTION A

1. The resistance of a $0.1N$ solution of sodium chloride in an electrolytic cell, with the area of the electrode being 1.50 cm^2 and the distance between them 0.75 cm , is equal to 46.8 ohms . Determine the specific and equivalent conductances of sodium chloride.

2*. Two electrodes having an area of 4 cm^2 are dipped into a 20 per cent solution of calcium chloride, the distance between them being 0.65 cm . A potential difference of 0.565 V is applied to the electrodes.

Determine the current in the circuit if the equivalent conductance of the solution is $40.6 \text{ ohm}^{-1} \cdot \text{g-eq}^{-1} \cdot \text{cm}^2$.

3. The equivalent conductance of barium chloride is equal to $123.94 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g-eq}^{-1}$.

Determine the resistance in a cell filled with a $0.01N$ solution of barium chloride if the area of the electrodes is 0.865 cm^2 and the distance between them, 0.258 cm .

4. After the titration of 100 ml of a solution of acetic acid with a $0.5N$ solution of sodium hydroxide the following data were obtained:

| | | | | | | | | |
|------------------------------------|------|------|------|------|------|------|------|------|
| Volume of $0.5N$ NaOH solution, | | | | | | | | |
| ml | 8.0 | 9.0 | 10.0 | 11.0 | 12.0 | 13.0 | 15.0 | 17.0 |
| Resistance, ohms | 75.0 | 68.1 | 62.3 | 57.0 | 53.2 | 50.8 | 51.5 | 52.1 |

Determine the normality of acetic acid.

5. On titration of 50 ml of hydrochloric acid with a $2N$ solution of potassium hydroxide the following results were obtained:

| | | | | | | |
|--|-----|------|------|------|------|------|
| Volume of $2N$ KOH solution, ml | 3.2 | 6.0 | 9.2 | 15.6 | 20.0 | 23.5 |
| Conductivity, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. . | 3.2 | 2.56 | 1.86 | 1.64 | 2.38 | 2.96 |

Find the normality of hydrochloric acid.

6. When 25 ml of a barium chloride solution was titrated conductometrically with a $0.55N$ solution of sulphuric acid, the following readings were obtained on a Kohlrausch bridge, the length of the bridge being 100 cm (a fixed resistance of 50.0 ohms was connected to the input terminal of the bridge):

Volume of 0.55*N*

| | | | | | | | | |
|---|------|------|------|------|------|------|------|------|
| H ₂ SO ₄ , ml . . . | 3.10 | 3.68 | 4.50 | 5.15 | 6.03 | 6.50 | 6.87 | 7.21 |
| Reading, cm . . . | 58.1 | 61.0 | 65.5 | 68.1 | 65.7 | 58.5 | 53.8 | 50.0 |

Plot the titration curve and determine the normality of the barium chloride solution and the accuracy of the titration.

7. When 25 ml of a mixture of hydrochloric and acetic acids was titrated with a 0.105*N* solution of sodium hydroxide the following readings were obtained on the scale of a high-frequency titration unit:

Volume of 0.105*N* NaOH

| | | | | | | | | | | | | | | |
|------------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| solution, ml | 2 | 4 | 5 | 6 | 7 | 8 | 9 | 11 | 13 | 15 | 16 | 17 | 18 | 19 |
| Instrument reading . . | 62 | 51 | 37 | 32 | 23 | 21 | 23 | 26 | 31 | 37 | 37 | 44 | 56 | 68 |

Find the concentrations of these acids (in g/litre).

SECTION B

8. The resistance of a 10 per cent solution of sulphuric acid in an electrolytic cell is 0.342 ± 0.002 ohm.

Find the conductivity and the equivalent conductance if the area of the electrodes is 5.25 ± 0.05 cm² and the distance between them, 0.65 ± 0.02 cm. The density of the solution is 1.07 ± 0.02 g/cm³. Which of the measurements gives the largest error? Calculate the accuracy of the determination of the conductance.

9*. To determine the constant of a cell, it was filled at 20 °C with a 0.1000*M* solution of potassium chloride, whose tabulated resistivity is 0.0117 ohm⁻¹·cm⁻¹. The resistance of the cell was found to be 324.2 ohms. After the cell was filled with a 0.050*N* solution of sulphuric acid the resistance was found to be equal to 1305.5 ohms.

Determine the equivalent conductance of the sulphuric acid solution.

10. The equivalent conductance of a 1.03×10^{-3} *N* solution of acetic acid at 25 °C is 48.15 ohm⁻¹·g-eq⁻¹·cm².

Determine the dissociation constant of acetic acid if the conductance of acetic acid at infinite dilution is 390.6 ohm⁻¹·cm²·g-eq⁻¹.

11*. The conductivity of water at 18 °C is $(4.00 \pm 0.05) \times 10^{-8}$ ohm⁻¹·cm⁻¹. The conductivity of a saturated solu-

tion of silver chloride in the same water is $(1.37 \pm \pm 0.05)10^{-6} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

Calculate the solubility of silver chloride under these conditions and find the calculation error.

12. The relation between the conductivity of hydrofluoric acid and its concentration is characterized by the following data:

| | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|------|
| Concentration, mole/litre | 0.004 | 0.007 | 0.015 | 0.030 | 0.060 | 0.120 | 0.240 | 0.480 | 1.50 |
| Conductivity $\chi \cdot 10^4$, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$ | 2.5 | 3.8 | 5.0 | 8.0 | 12.3 | 21 | 36 | 67 | 200 |

Draw a plot of conductance versus concentration. Deduce the equation of the straight-line portion. Using the graph and the derived equation, determine the concentration of the solution if its conductivity is equal to $45 \times 10^{-4} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

13*. Solutions of sodium hydroxide of varying concentration have the following conductances in a given cell:

| | | | | | |
|--|------|------|------|------|------|
| Concentration of NaOH solutions, per cent by weight | 4 | 6 | 8 | 10 | 15 |
| Conductance, ohm^{-1} | 1628 | 2242 | 2729 | 3093 | 3490 |

A 200-ml volume of a solution having a conductance of 1850 ohm^{-1} was mixed with 300 ml of a solution with a conductance of 3200 ohm^{-1} .

Determine the conductance of the resulting solution in the same cell and its normality.

14. On titration of 200 ml of a mixture of potassium hydroxide and ammonium hydroxide with a $0.2N$ hydrochloric acid the following readings were obtained on the galvanometer of a high-frequency titration unit:

| | | | | | | | | | | | | | |
|-------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Volume, ml | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 4.0 | 5.0 | 6.0 | 7.0 | 7.5 | 8.0 | 8.5 |
| Galvanometer reading | 42 | 39 | 29 | 23 | 21 | 14 | 20 | 22 | 23 | 25 | 30 | 44 | 57 |

Plot a titration curve and find the concentrations of KOH and NH_4OH . Determine the amounts of $0.1N$ solutions of potassium hydroxide and ammonium hydroxide that are required for preparing 200 ml of the indicated solution.

15*. A conductance-measuring instrument filled at 18°C with a 0.1*N* solution of potassium chloride has a resistance of 79 ohms and the one filled with a 0.105*N* acetic acid solution has a resistance of 179 ohms.

Determine the dissociation constant of acetic acid.

SECTION C

16. Calculate the equivalent conductance of a solution of AgIO₃ at infinite dilution if the values of this quantity are known for the following solutions: NaIO₃, $\lambda_{\infty} = 90.1$; CH₃COONa, $\lambda_{\infty} = 91.0$; CH₃COOAg, $\lambda_{\infty} = 103.0$.

17. The conductivity of ethylamine, C₂H₅NH₂OH, on dilution of 1 mole in 16 litres is equal to $1.312 \times 10^{-3} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

Determine the dissociation constant of ethylamine if the mobility of the ion C₂H₅NH₃⁺ is 58.6. Estimate the accuracy of this calculation if the conductivity was measured with an accuracy of up to $0.002 \times 10^{-3} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

18*. The resistance of a saturated solution of silver chloride in a cell is 52.50 ± 0.05 ohms and that of water under the same conditions is 112.00 ± 0.05 ohms. The temperature of the experiment is 25 °C.

Calculate the solubility and the solubility product of silver chloride if the cell constant is $0.18 \pm 0.02 \text{ cm}^{-1}$. Calculate the accuracy of the determination and find the value that gives the largest error.

19. A conductometric cell with 25 ml of a sodium hydroxide solution is inserted into a circuit having a fixed resistance of 100 ohms, a milliammeter and a 5.85-V storage battery. In the course of the titration with 0.105*N* hydrochloric acid the following current was measured and the following results obtained:

| | | | | | | | |
|--|------|------|------|------|------|------|------|
| Volume of 0.105 <i>N</i> hydrochloric acid, ml | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Current, mA | 45.6 | 48.7 | 51.4 | 51.2 | 51.4 | 47.1 | 39.3 |

Plot a titration curve of the conductivity against the volume (with account taken of dilution) and determine the concentration of sodium hydroxide. Find the accuracy of the calculation and the source of the largest error if the

measuring accuracy for volume is 0.05 ml, for voltage, 0.02 V and for current, 0.1 mA.

20. On titration of 20 ml of a 0.042*M* solution of $\text{SnBr}_2\text{F}_{10}$ in BrF_3 with a 0.02*M* solution of KBrF_4 the following readings were obtained on the slidewire scale of a Kohlrausch bridge (the cell is connected to the bridge input terminal):

| | | | | | | |
|---|------|------|------|------|------|------|
| Volume of 0.02 <i>M</i> solution of | | | | | | |
| KBrF_4 , ml | 0 | 1.0 | 2.0 | 2.5 | 3.0 | 3.5 |
| Reading, cm | 61.0 | 58.1 | 52.6 | 50.5 | 45.9 | 39.2 |
| Volume of 0.02 <i>M</i> solution of KBrF_4 , | | | | | | |
| ml | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | |
| Reading, cm | 30.8 | 29.6 | 31.9 | 34.0 | 35.3 | |

Plot a titration curve and draw a conclusion as to the reaction taking place during the titration.

21. The conductivity of sea water at 25 °C obeys the following empirical law:

$$\chi = 1.82 \times 10^{-3}C - 1.28 \times 10^{-5}C^2 + 1.18 \times 10^{-7}C^3$$

where C is the concentration in grams per kilogram.

The conductivity of pure sea water is $4.62 \times 10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. The conductivity of the water at the mouth of a river equals $1.55 \times 10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

Find the ratio in which the river water mixes with sea water if the conductivity of the former may be neglected. What is the value of this quantity for water in which the ratio of sea to river water is 1 : 5?

22. On titration of 10 ml of a 0.015*M* solution of tetramethylammonium sulphite in liquid sulphur dioxide with a 0.060*M* solution of thionyl chloride the following values of conductivity were obtained:

| | | | | | | | | |
|--|------|------|------|------|------|------|------|------|
| Volume of 0.060 <i>M</i> thionyl | | | | | | | | |
| chloride solution, ml | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | |
| Conductivity, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$ | 1.24 | 1.11 | 0.99 | 0.85 | 0.71 | 0.58 | 0.61 | |
| Volume of 0.060 <i>M</i> | | | | | | | | |
| thionyl chloride | | | | | | | | |
| solution, ml . . | 3.5 | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 | 7.0 |
| Conductivity, | | | | | | | | |
| $\text{ohm}^{-1} \cdot \text{cm}^{-1}$. . | 0.63 | 0.65 | 0.66 | 0.67 | 0.70 | 0.96 | 1.11 | 1.26 |

Plot a titration curve and draw a conclusion as to the processes occurring during the titration.

23*. The conductivity of the sulphuric acid used in a technological process is $4.58 \times 10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. The conductivity of a given acid is $1.8 \times 10^{-1} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$.

How many kilograms of this acid must be added to 500 litres of water to produce the desired concentration?

24*. A portion of codeine weighing 20 mg was dissolved in 25 ml of glacial acetic acid. The resistance of the resulting solution in a cell is 1920 ohms; the area of the electrodes is 4 cm^2 and the distance between them, 0.65 cm.

Determine whether the codeine contains current-conducting impurities (extraneous salts) if the electrical conductivity of pure codeine in acetic acid at different concentrations is as follows:

| | | | | |
|---|------|-------|-------|-------|
| $C \times 10^4$, g-eq/litre | 63.2 | 31.6 | 15.8 | 7.90 |
| $\chi \times 10^6$, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$ | 1.19 | 0.797 | 0.533 | 0.371 |

25. The capacity of an electrolytic cell is 25 ml. On calibration against a 0.1N potassium chloride solution at 25 °C the resistance of the cell was found to be equal to 24.2 ohms. The resistance of the cell filled with a solution of barium hydroxide was found to equal $4.36 \times 10^{-2} \text{ ohm}$. After 0.5 litre of air was passed through the cell its resistance fell to $3.38 \times 10^{-2} \text{ ohm}$.

Determine the content of carbon dioxide in the air (in per cent by volume) if in the concentration range of interest the molar conductance of $\text{Ba}(\text{OH})_2$ is equal to $410 \text{ ohm}^{-1} \cdot \text{mole}^{-1} \cdot \text{cm}^2$.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. What are the advantages and disadvantages of direct conductometric analysis as applied to solutions?

(a) Its advantage lies in the fact that only one measurement is required, and its disadvantage is that very precise thermostating is needed since electrical conductivity is strongly dependent on temperature.

(b) The concentration in this method is determined by a single measurement of conductivity, but it changes greatly in the presence of extraneous salts and that is why this method is applicable only to pure one-component solutions.

(c) This method has no advantages over the conductometric titration, and the main disadvantage is that it requires more complicated apparatus than conductometric titration.

(d) An advantage of direct conductometric analysis is that the apparatus needed is more simple than that used

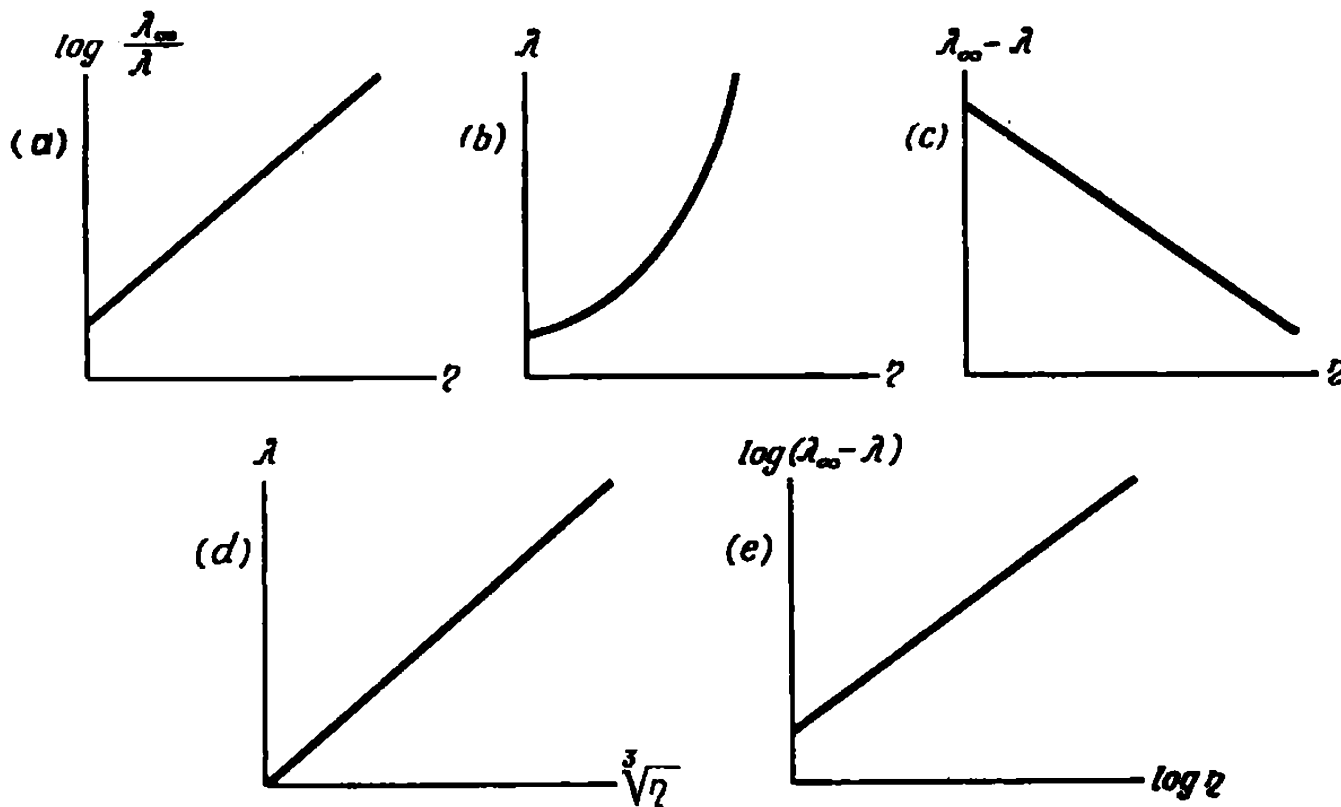


Figure 52

in conductometric titration. Its disadvantage is the absence of a direct proportionality between the concentration of the unknown substance and conductivity.

(e) It is faster, but the unknown concentration can be determined from conductivity for concentrated electrolytes only.

2. Can the method of direct conductometric analysis be used to determine oxidants and reductants and conductometric titration for titrating by the oxidation-reduction method?

(a) Both methods can be used to determine oxidants or reductants.

(b) Direct conductometric analysis may be used and conductometric titration may not, since oxidation-reduction reactions are always carried out in the presence of other foreign ions, particularly hydrogen ions.

(c) Direct conductometry may be used for determination of the concentration of pure solutions of oxidants or reductants but conductometric titration may not, since in the

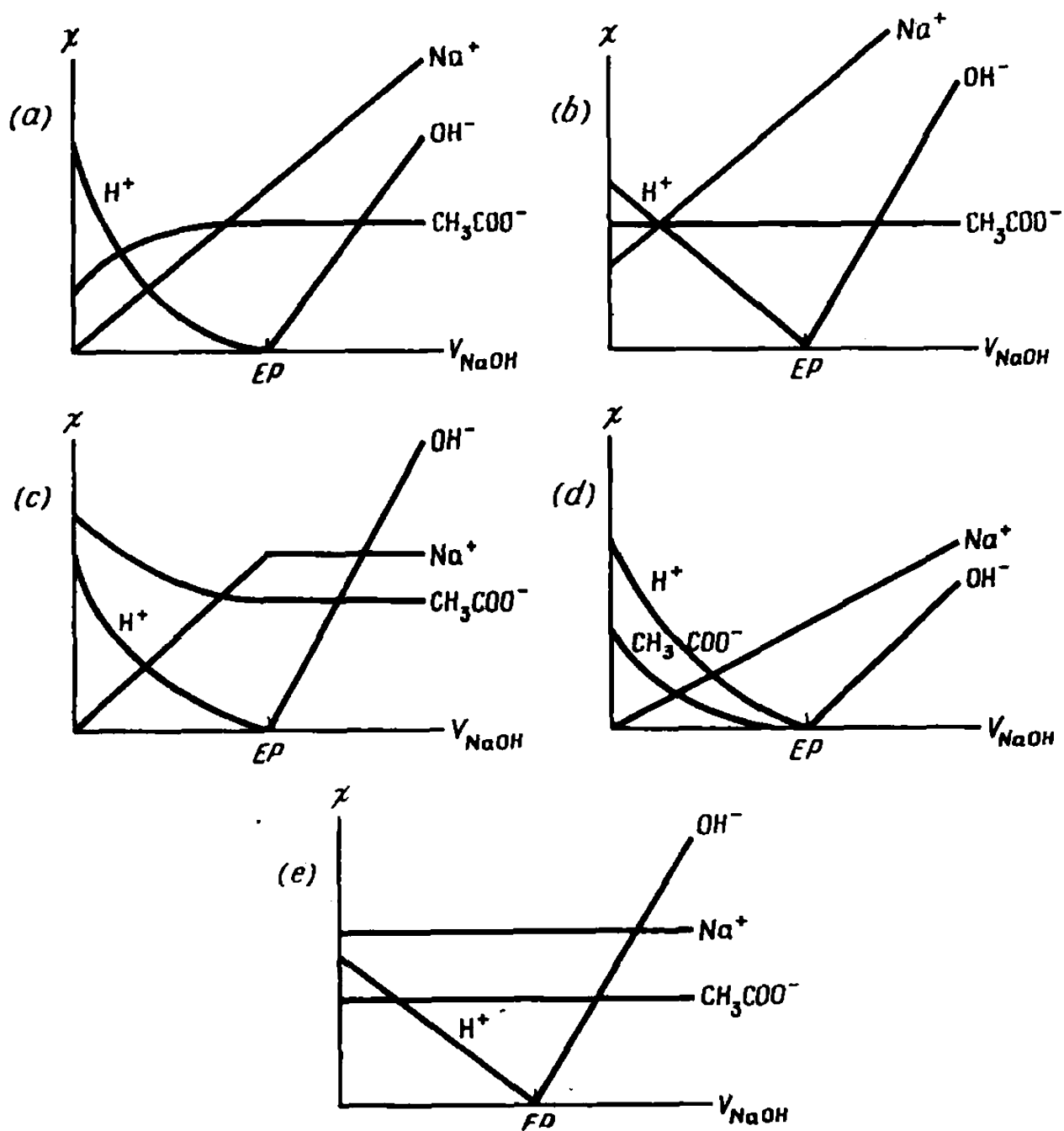


Figure 53

course of oxidation-reduction reactions the electrical conductivity varies insignificantly and the determination of the equivalence point is not precise.

(d) Direct conductometry cannot be used in this case since the oxidants will react with the electrodes. Conductometric titration may be used since in this case the interaction with the electrode will not affect the titration results.

(e) Neither of these methods can be used for analysis of oxidants and reductants.

3. Which of the graphs given in Fig. 52 reflects correctly the dependence of equivalent conductance λ or its function on the concentration η in g-eq/ml?

4. Which of the graphs given in Fig. 53 reflects correctly the change in the contribution of each of the ions involved to the overall conductance of the solution during the titration of acetic acid with sodium hydroxide?

5. Which of the graphs given in Fig. 54 reflects correctly the change of the contribution of each of the ions involved to the total conductance of the solution during the titration of a mixture of KI and KCl with silver nitrate if $SP_{AgI} \ll \ll SP_{AgCl}$?

6. The resistance of a 5 per cent (by weight) solution of KCl (molecular weight 74.5) in a cell is 28 ohms if the area of the electrodes is 1.5 cm^2 and the distance between them, 0.5 cm. Which of the following formulas should be used to calculate the equivalent conductance of the solution?

$$(a) \quad \lambda = \frac{1/28}{74.5 \times 5/95} = 0.0068.$$

$$(b) \quad \lambda = \frac{0.5/1.5 \times 28}{5 \times 1000/95 \times 74.5} = 0.017.$$

$$(c) \quad \lambda = \frac{0.5/1.5 \times 28}{5/95 \times 74.5} = 17.$$

$$(d) \quad \lambda = \frac{1.5 \times 28/0.5}{5/95 \times 74.5} = 1.23 \times 10^5.$$

$$(e) \quad \lambda = \frac{1.5 \times 28/0.5}{5 \times 1000/95 \times 74.5} = 123.$$

7. Indicate the answers that characterize correctly the difference between conductometric titration and various high-frequency titration methods.

(a) In high-frequency titration methods the readings depend not only on electrical conductance but also on the dielectric constant and magnetic permeability of the solution and obey more complex relationships.

(b) The data of high-frequency titrations are independent of temperature.

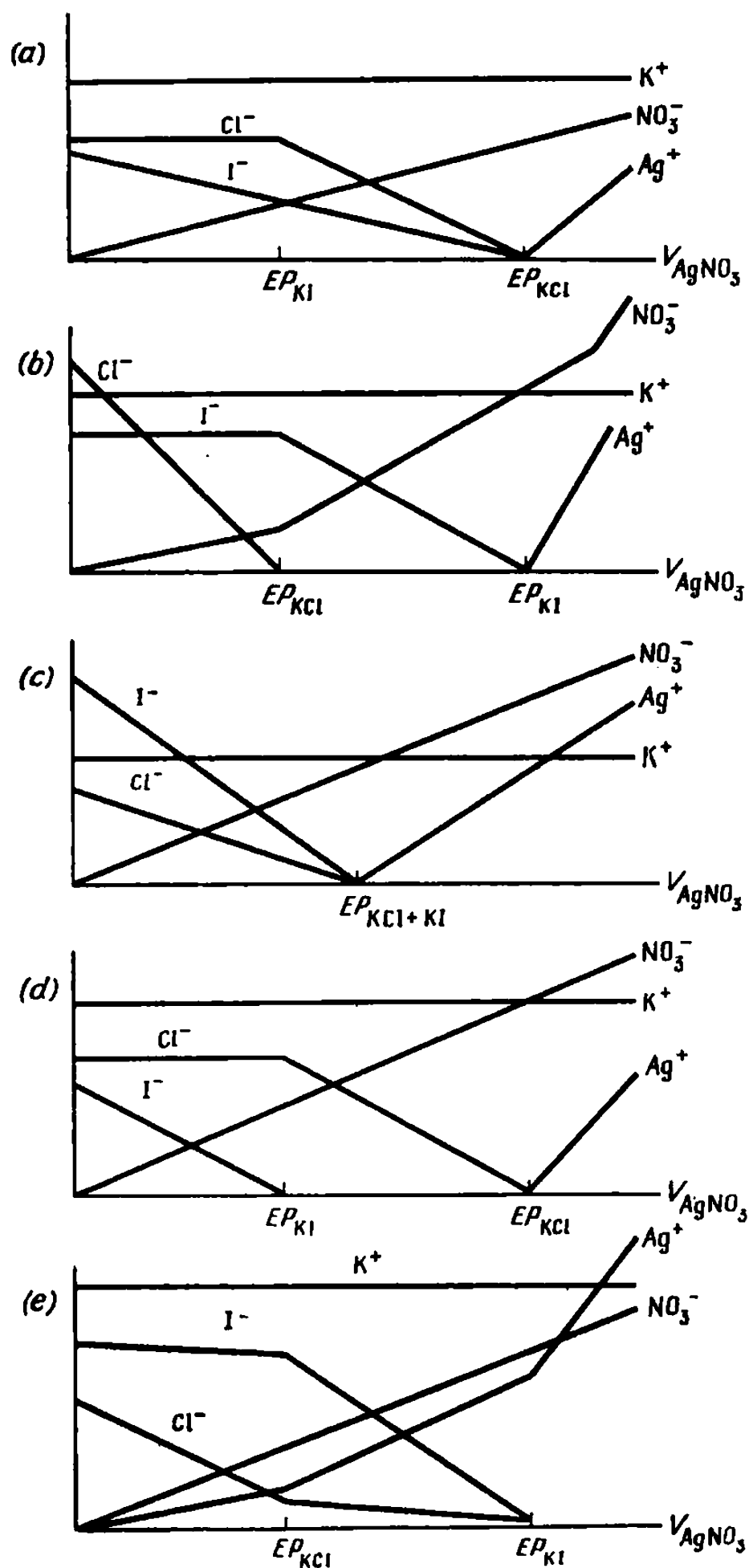


Figure 54

(c) In Z-metric titration, just as in conductometric titration, only the electrical conductance is studied and therefore it does not differ from the conductometric titration.

(d) All high-frequency titration methods are faster than conductometric titrations.

(e) In Z-metric titration, use is made of the effect of varying dielectric properties of the solution on the frequency of the oscillations generated.

(f) All high-frequency titration methods are more sensitive to impurities than conductometric titrations.

(g) In a high-frequency titration, the electrodes may be placed outside the solution being analysed.

(h) In Q-metric methods, use is made of the effect of the cell on the electrical parameters of the generator. The titration curve is plotted on the basis of the readings of grid or anode current and of the volume of the reagent.

(i) High-frequency titration methods are more accurate than the methods of conductometric titration.

(j) In F-metric methods, use is made of the effect of the electrical conductance and magnetic permeability of the solution on the frequency of the oscillations generated.

8. Find under B the definitions of the types of electrical conductance corresponding to the symbols given under A.

A

(a) λ_{∞} ; (b) μ ; (c) λ ; (d) χ ; (e) w .

B

(1) This is the reciprocal of specific resistance.

(2) This is the conductivity referred to the number of gram-equivalents in the volume under study.

(3) This is the conductivity referred to the number of gram-moles in 1 cm³ of the solution.

(4) This is the conductivity referred to the concentration of the solution in moles per litre.

(5) This is the equivalent conductance at an infinitely small concentration of the solution.

(6) This is a quantity directly proportional to the total resistance of the solution.

(7) This is the equivalent conductance at an infinitely low temperature; it depends only on the nature of the solution.

(8) This is the conductivity divided by the concentration in gram-equivalents per millilitre.

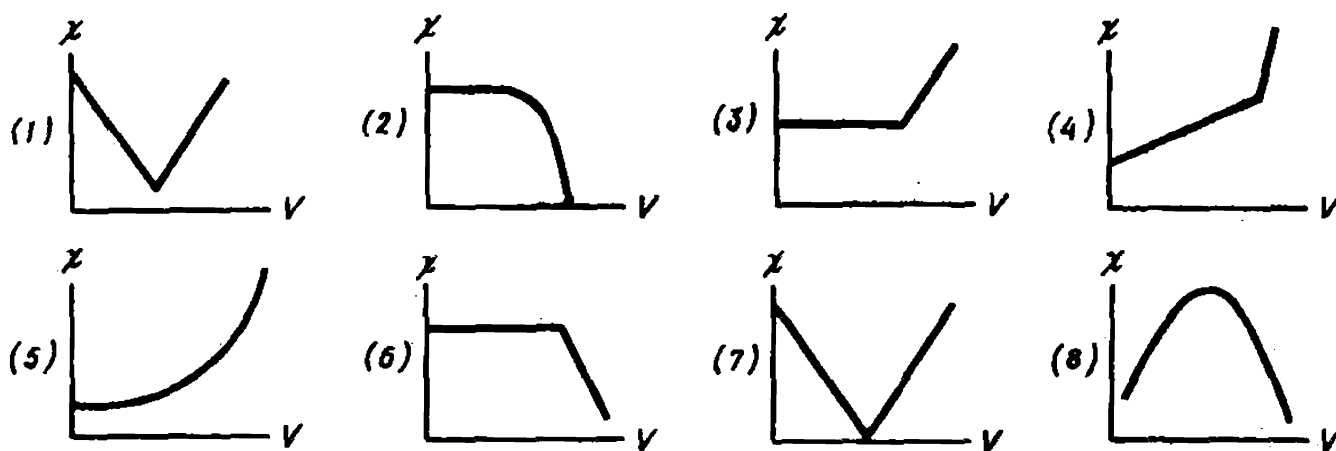
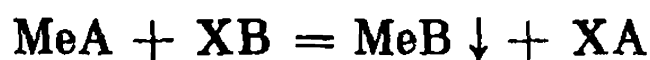


Figure 55

9. Indicate the conditions under which a conductometric titration by the precipitation method using the reaction



would yield the titration graphs shown in Fig. 55 (U is the ionic mobility).

(a) If U_{Me} is equal to U_{X} and the MeB precipitate is sufficiently soluble.

(b) If U_{A} is greater than U_{B} .

(c) If U_{Me} is lower than U_{X} .

(d) If U_{Me} is equal to U_{X} .

(e) If U_{Me} is greater than U_{X} and the MeB precipitate is sufficiently soluble.

(f) If U_{A} is equal to U_{Me} .

(g) If U_{Me} is greater than U_{X} .

(h) If U_{A} is equal to U_{B} .

(i) If U_{Me} is greater than U_{X} .

(j) Such a graph cannot be obtained in a conductometric titration.

10. Using the handbook, indicate under B the values of specific conductance (conductivity) for the solutions listed under A.

| A | B |
|---|-----------------------------|
| (a) 20% CdI_2 at 18 °C. | (1) 93×10^{-4} , |
| (b) 5% $\text{Sr}(\text{NO}_3)_2$ at 15 °C. | (2) 4212×10^{-4} . |
| (c) 42% KOH at 15 °C. | (3) 2513×10^{-4} . |
| (d) 10% LiCl at 18 °C. | (4) 186×10^{-4} . |
| (e) 1 <i>N</i> KCl at 10 °C. | (5) 1.2×10^{-5} . |
| (f) Saturated NaCl at 25 °C. | (6) 1218×10^{-4} . |
| (g) Methyl nitrate at 25 °C. | (7) 309×10^{-4} . |
| (h) Dichlorohydrin at 25 °C. | (8) 4.5×10^{-5} . |

Potentiometry

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. Calculate the potential of a copper electrode in a solution which is $0.01M$ relative to copper chloride and $0.01M$ relative to copper sulphate at 30°C . What error will be introduced into the calculation if the activity coefficient of copper ions is ignored?

Solution: The potential of the copper electrode is calculated from the Nernst equation

$$E = E^0 + \frac{2.3RT}{nF} \log C$$

where E^0 is the standard redox potential of the pair $\text{Cu}^{2+}/\text{Cu}^0 = +0.340\text{ V}$; n is the number of electrons; C is the concentration of copper ions; $2.3RT/F$ at 30°C is equal to 0.060 .

Substituting the data given, we get

$$\begin{aligned} E &= 0.340 + \frac{0.060}{2} \log 0.02 = 0.340 + 0.030 (-1.70) = \\ &= 0.340 - 0.051 = 0.299\text{ V} \end{aligned}$$

To calculate the activity $a_{\text{Cu}^{2+}}$, we compute the ionic strength of the solution from the equation

$$\mu = \frac{1}{2} (C_{\text{Cu}^{2+}} \cdot z_{\text{Cu}^{2+}}^2 + C_{\text{Cl}^-} \cdot z_{\text{Cl}^-}^2 + C_{\text{SO}_4^{2-}} \cdot z_{\text{SO}_4^{2-}}^2) = 0.07$$

Referring to the handbook, we find the value of the activity coefficient for doubly charged ions:

$$f_{\text{Cu}^{2+}} = 0.453$$

Substituting the data obtained into the Nernst equation, we calculate the potential:

$$a = Cf = 0.02 \times 0.453 = 0.00906$$

$$E = 0.340 + \frac{0.060}{2} \log 0.00906 = 0.279 \text{ V}$$

Hence, if the ionic activity is ignored, the error will be
 $0.299 - 0.279 = 0.020 \text{ V}$

In direct potentiometric analyses such an error must not be neglected.

Example 2. Calculate the solubility product (SP) of silver chloride at 18 °C if the potential of a silver electrode dipped into a saturated solution of silver chloride is equal to 0.518 V versus the hydrogen electrode.

Solution: The potential of the silver electrode is

$$E = E^0 + 0.058 \log [\text{Ag}^+]$$

From relevant tables we find for silver $E^0 = 0.800 \text{ V}$.
Hence

$$0.518 = 0.800 + 0.058 \log [\text{Ag}^+]$$

$$0.058 \log [\text{Ag}^+] = -0.800 + 0.518 = -0.282$$

$$\log [\text{Ag}^+] = -\frac{0.282}{0.058} = -4.873$$

$$[\text{Ag}^+] = 1.34 \times 10^{-5} \text{ g-ion/litre}$$

$$\text{SP} = (1.34 \times 10^{-5})^2 = 1.79 \times 10^{-10}$$

Example 3. The electromotive force (emf) of the cell

$\text{Pt}(\text{H}_2) \mid \text{acid solution} \parallel 1N \text{ calomel half-cell}$

at 28 °C is equal to 0.571 V.

Calculate the concentration of hydrogen ions and the pH of the solution.

Solution: The emf is given by

$$E = E_{\text{NCE}} = E_{\text{H}}$$

Hence

$$E_{\text{H}} = E_{\text{NCE}} - E \quad E_{\text{NCE}} = 0.2821 \text{ V}$$

$$E_{\text{H}} = 0.2821 - 0.5710 = -0.2889 \text{ V}$$

$$E_H = -0.059 \log [H^+] = 0.059 \text{pH} = 0.2889$$

$$\text{pH} = \frac{0.2889}{0.059} = 4.88; \quad C_{H^+} = 1.32 \times 10^{-5} \text{ g-ion/litre}$$

Example 4. Determine the potential of a quinhydrone electrode, E_{QE} , on titration of a 0.1*N* solution of benzoic acid with a 0.1*N* solution of NaOH at the point where 90 per cent of the acid will have been titrated and at the point of equivalence. Use a 1*N* calomel half-cell as a reference electrode; the temperature is 20 °C. Take into account the dilution of the solution.

Solution: When 90 per cent of the benzoic acid is titrated, the solution will be a buffer mixture consisting of a 0.09/1.9*N* solution of sodium benzoate and a 0.01/1.9*N* solution of benzoic acid. The pH value at this point is calculated from the formula

$$\text{pH} = \text{pK}_{\text{acid}} + \log \frac{C_{\text{salt}}}{C_{\text{acid}}}$$

For benzoic acid the table value of pK is 4.70. Hence

$$\text{pH} = 4.70 + \log (0.09/0.01) = 4.70 + 0.96 = 5.66$$

$$E = E_{QE} = 0.058 \text{pH} - E_{NCE}$$

From the formula we find that at 20 °C

$$E_{QE} = 0.703 \text{ V} \quad \text{and} \quad E_{NCE} = 0.284 \text{ V}$$

Consequently

$$E = 0.703 - 0.058 \times 5.66 - 0.284 = 0.091 \text{ V}$$

The pH value for sodium benzoate at the equivalence point is calculated from the formula for the salt of a weak acid and a strong base:

$$\text{pH} = 7 + \frac{1}{2} \text{pK}_{\text{acid}} + \frac{1}{2} \log C_{\text{salt}}$$

$$\text{pH} = 7 + \frac{1}{2} \times 4.70 + \frac{1}{2} \log 0.05 = 7 + 2.35 - 0.65 = 8.70$$

The concentration of the salt has been calculated with the dilution taken into account.

Hence

$$E = 0.703 - 0.058 \times 8.70 - 0.284 = -0.086 \text{ V}$$

Example 5. When 1.5 ml of a 0.01*N* hydrochloric acid was added to 100 ml of a hydrochloric acid solution containing carbonic acid, the potential of the indicator quinhydrone electrode changed from 190 to 210 mV.

Calculate the concentration of hydrochloric acid in the solution if the temperature of the experiment is 25 °C.

Solution: We set up two equations for calculating the potential before and after the addition of the solution:

$$E_1 = E^0 - 0.059 \text{pH}_1 = E^0 + 0.059 \log C_{\text{H}^+}$$

$$E_2 = E^0 - 0.059 \text{pH}_2 =$$

$$= E^0 + 0.059 \log \left(C_{\text{H}^+} \frac{100}{100 + 1.5} + \frac{1.5 \times 0.01}{101.5} \right)$$

$$E_2 - E_1 = 20 \text{ mV} = 0.02 \text{ V}$$

$$0.02 = 0.059 [\log (0.985 C_{\text{H}^+} + 1.48 \times 10^{-4}) - \log C_{\text{H}^+}] =$$

$$= 0.059 \log \left(0.985 + \frac{1.48 \times 10^{-4}}{C_{\text{H}^+}} \right)$$

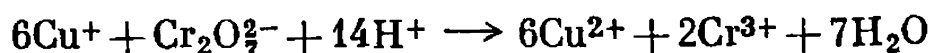
$$\frac{0.02}{0.059} = 0.338 = \log \left(0.985 + \frac{1.48 \times 10^{-4}}{C_{\text{H}^+}} \right)$$

$$0.985 + \frac{1.48 \times 10^{-4}}{C_{\text{H}^+}} = 2.170$$

$$C_{\text{HCl}} = C_{\text{H}^+} = \frac{1.48 \times 10^{-4}}{1.185} = 1.249 \times 10^{-4} \text{ g-eq/litre}$$

Example 6. Construct a curve for the titration of 100 ml of a 0.1*N* solution of Cu_2SO_4 ($E^0 = 0.153$) with a 0.1*N* solution of potassium dichromate ($E^0 = 1.333$).

Solution: The following reaction takes place during titration:



We calculate the potentials during the titration from the equation

$$E = 0.153 + \frac{0.058}{1} \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]}$$

| | | | | | |
|-------------------------------------|-------|-------|-------|-------|--------|
| Volume of $K_2Cr_2O_7$ solution, ml | 10 | 50 | 90 | 99 | 99.9 |
| $[Cu^{2+}]$, mole/litre | 0.001 | 0.05 | 0.09 | 0.099 | 0.0999 |
| $[Cu^+]$, mole/litre | 0.099 | 0.05 | 0.01 | 0.001 | 0.0001 |
| E , V | 0.098 | 0.153 | 0.211 | 0.269 | 0.327 |

The potential at the equivalence point is given by

$$E = \frac{0.153 + 6 \times 1.333}{6 + 1} = 1.164$$

Now we calculate the potential after the equivalence point for the redox reaction

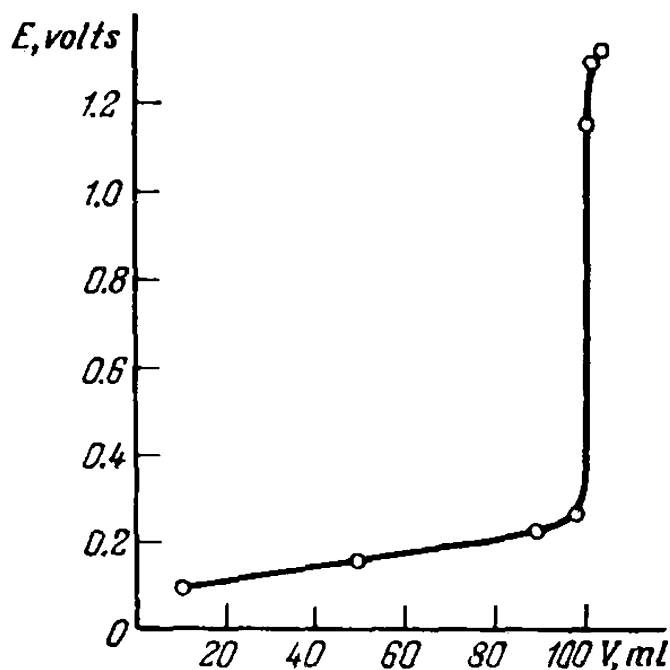
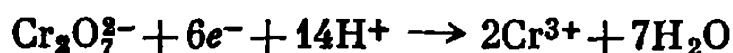


Figure 56

The concentration of Cr^{3+} ions is assumed to be constant and equal to $0.1N$.

$$E = 1.333 + \frac{0.058}{6} \log \frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]^2}$$

| | | | |
|-------------------------------------|-----------|-----------|-----------|
| Volume of $K_2Cr_2O_7$ solution, ml | 100.01 | 100.1 | 101 |
| $[Cr_2O_7^{2-}]$, mole/litre | 10^{-5} | 10^{-4} | 10^{-3} |
| $[Cr^{3+}]$, mole/litre | 0.1 | 0.1 | 0.1 |
| E , V | 1.293 | 1.303 | 1.313 |

On the basis of the data obtained we construct the titration curve (see Fig. 56).

2. MULTIVARIANT PROBLEMS

1*. Calculate the potential of a metal electrode with respect to a reference electrode under the conditions indicated (see Table 37).

TABLE 37

| Variant | Electrode | Volume of electrolyte, ml | Solute and its amount | Temperature, °C | Reference electrode |
|---------|-----------|---------------------------|--|-----------------|----------------------------------|
| I | Copper | 1000 | CuSO ₄ , 16 g | 18 | Hydrogen |
| II | Zinc | 500 | ZnSO ₄ , 0.1 g-eq | 18 | Calomel (0.1N NCE) |
| III | Nickel | 1000 | NiCl ₂ , 0.5 g-eq | 30 | Saturated calomel |
| IV | Aluminium | 200 | AlCl ₃ , 27 g | 30 | Saturated calomel |
| V | Silver | 400 | AgNO ₃ , 0.2 g-eq | 25 | Calomel (1N NCE) |
| VI | Cadmium | 1000 | Cd(NO ₃) ₂ , 18.8 g | 25 | Hydrogen |
| VII | Iron | 100 | FeSO ₄ ·7H ₂ O, 20.5 g | 30 | Calomel (0.1N NCE) |
| VIII | Cobalt | 200 | CoCl ₂ , 0.15 g-eq | 25 | Silver-silver chloride in 1N HCl |

The potentials of the comparison electrodes should be calculated from the following formulas:

| | |
|---|--|
| Saturated calomel electrode | $E = 0.2438 + 6.5 \times 10^{-4} (25 - t) \text{ V}$ |
| Normal calomel electrode | $E = 0.2828 + 2.4 \times 10^{-4} (25 - t) \text{ V}$ |
| Decinormal calomel electrode | $E = 0.3365 + 0.6 \times 10^{-4} (25 - t) \text{ V}$ |
| Quinhydrone electrode | $E = 0.6990 + 7.4 \times 10^{-4} (25 - t) \text{ V}$ |
| Mercury-mercurous sulphate electrode | $E = 0.6151 + 8 \times 10^{-4} (25 - t) \text{ V}$ |
| Silver-silver chloride (1N) electrode | $E = 0.2223 + 6.4 \times 10^{-4} (25 - t) \text{ V}$ |
| Silver-silver chloride (0.1N) electrode | $E = 0.2895 + 0.5 \times 10^{-4} (25 - t) \text{ V}$ |

(Use these formulas for calculating electrode potentials in all other problems of this section.)

2. Calculate the pH of a solution from the data listed in Table 38.

TABLE 38

| Variant | Electrode | | Temperature, °C | Emf, V |
|---------|-------------|------------------------------------|-----------------|--------|
| | indicator | reference | | |
| I | Hydrogen | Calomel (0.1N NCE) | 30 | 0.624 |
| II | Quinhydrone | Calomel (1N NCE) | 25 | 0.154 |
| III | Hydrogen | Silver-silver chloride in 0.1N HCl | 20 | 0.505 |
| IV | Hydrogen | Mercury-mercurous sulphate | 25 | 1.146 |
| V | Quinhydrone | Silver-silver chloride in 1N KCl | 20 | 0.248 |
| VI | Hydrogen | Saturated calomel | 35 | 0.527 |
| VII | Quinhydrone | Saturated calomel | 40 | 0.205 |
| VIII | Quinhydrone | Mercury-mercurous sulphate | 18 | -0.086 |

3*. Calculate the potential of a system at 20 °C in the course of titration at the indicated moment with dilution taken into account if a 0.1N solution is titrated (see Table 39).

TABLE 39

| Variant | Titrate | Titrant | Moment of titration |
|---------|--------------------------------|---|--|
| I | HCl | NaOH | 75 per cent acid titrated |
| II | NH ₄ OH | H ₂ SO ₄ | At the equivalence point |
| III | CH ₃ COOH | NH ₄ OH | At the equivalence point |
| IV | H ₃ BO ₃ | NaOH | 50 per cent acid titrated |
| V | FeSO ₄ | KBrO ₃ | At the equivalence point |
| VI | KMnO ₄ | CrSO ₄ | 99 per cent KMnO ₄ titrated |
| VII | KI | K ₂ Cr ₂ O ₇ | 75 per cent KI titrated |
| VIII | KClO ₃ | HAsO ₂ | At the equivalence point |

4*. Plot the potential change curves at 20 °C for the titration of the systems indicated in Table 40. In the titration by the neutralization method use is made of a quinhydrone and a 0.1N calomel electrode, and when the redox method is employed, a platinum and a saturated calomel electrode are used.

TABLE 40

| Variant | Titrate | Titrant |
|---------|--|-------------------------------|
| I | 0.1N H_2SO_4 | 1N NaOH |
| II | 1N $\text{C}_6\text{H}_5\text{COOH}$ | 1N KOH |
| III | 1N H_3AsO_4 | 1N NaOH (all titration jumps) |
| IV | 0.1N $\text{CO}(\text{NH}_2)_2$ | 0.1N CH_3COOH |
| V | 0.1N Na_2SO_3 | 0.1N KIO_3 |
| VI | 1N KBrO | 1N CrSO_4 |
| VII | A mixture of equal volumes of 0.1N H_2SO_4 and 0.1N ClH_2CCOOH | 0.1N KOH |
| VIII | A mixture of equal volumes of 0.1N VSO_4 and CuSO_4 | 0.1N FeSO_4 |

3. PROBLEMS

SECTION A

1*. Calculate the potential of a cadmium electrode in a 0.05N solution of cadmium nitrate relative to the hydrogen electrode at 25 °C.

2*. Calculate the potential of an aluminium electrode in a solution containing 13.35 g of aluminium chloride in 500 ml of the solution, relative to the hydrogen and the saturated calomel electrode at 30 °C.

3*. Calculate the potential of a quinhydrone electrode in a solution with $\text{pH} = 5.7$ relative to the calomel electrode (0.1N NCE) at 18 °C.

4. The potential difference between the hydrogen electrode and the saturated calomel electrode dipping into an acidic solution is 0.435 V at 25 °C.

Determine the pH of the solution.

5*. Calculate the potential of a platinum electrode in a solution containing 19.5 g of potassium chromate and 15.8 g of chromium chloride in 200 ml, relative to the calomel electrode (0.1N NCE) at the temperature of the solution 18 °C.

6*. To a 0.05N solution of lead nitrate is added an equivalent amount of potassium iodide.

Calculate the potential of a lead electrode relative to the normal calomel electrode if the temperature of the experiment is 30 °C.

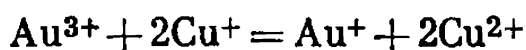
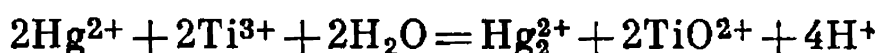
7*. The emf of the cell $\text{Ag} | \text{AgNO}_3 || \text{calomel electrode}$ (0.1N NCE) at 18 °C is 350 mV.

Determine the concentration of silver nitrate in the solution (in mole/litre).

8*. By how many millivolts will the potential of a hydrogen electrode change relative to the calomel electrode (0.1N NCE) if 20 ml of a 0.2N ammonia solution is mixed with 50 ml of a 0.1N solution of HCl? The temperature of the experiment is 20 °C.

9*. Calculate the potential on titration of a 0.05N phenol solution with a 0.1N solution of KOH at the equivalence point and at the point where 50 per cent of phenol has been titrated. The indicator electrode used is a quinhydrone electrode and the reference electrode is a saturated calomel electrode. The temperature of the experiment is 18 °C.

10*. Compute the potential at 20 °C at the equivalence point and the value of potential jump on the titration curve to within ± 0.1 per cent (before and after the point of equivalence) for the reactions



11*. Plot the potential change curve at 20 °C for precipitation of Ag_2CrO_4 from a 1N solution of silver nitrate with a 1N potassium chromate solution if the initial volume of the silver nitrate solution was 100 ml and $\text{SP}_{\text{Ag}_2\text{CrO}_4} = 9.0 \times 10^{-12}$.

12*. Plot the potential change curve at 20 °C for titration of 200 ml of a 0.1N solution of iron(II) sulphate with a 1N solution of potassium bromate.

13*. Compute the potentials at the points of equivalence and find out whether the components of a mixture of $\text{Cr}_2\text{O}_7^{2-}$ and MnO_4^- and of I^- and IO_3^- can be potentiometrically titrated separately with a solution of iron(II) sulphate and a solution of a silver salt, respectively.

14*. Using the data on potentiometric titrations given below, construct the titration curves and determine the

volume of titrant at the equivalence point. The temperature of the experiments is 20 °C.

The ion $\text{Cr}_2\text{O}_7^{2-}$ is titrated with a Cr^{2+} ion:

| | | | | | | | | |
|--------------------|-----|-----|-----|-----|-----|------|------|------|
| V , ml | 0 | 0.5 | 1.0 | 2 | 3 | 4 | 5 | 5.5 |
| E , mV | 280 | 250 | 200 | 190 | 170 | 150 | 140 | 130 |
| V , ml | 5.7 | 5.8 | 5.9 | 6.0 | 6.2 | 6.3 | 6.4 | 6.5 |
| E , mV | 120 | 110 | 110 | 90 | 20 | -120 | -150 | -200 |

The Cr^{2+} ion is titrated with a MnO_4^- ion:

| | | | | | | | | | | |
|--------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| V , ml | 0 | 1 | 2 | 3 | 4 | 5 | 5.5 | 6 | 6.5 | 7.0 |
| E , mV | 285 | 295 | 305 | 320 | 335 | 360 | 400 | 620 | 641 | 658 |

These titrations are carried out in a 1*N* H_2SO_4 .

The KI-KCl mixture is titrated with a solution of AgNO_3 .

| | | | | | | | | | | | |
|--------------------|------|------|------|-------|-------|------|------|-------|-------|------|-----|
| V , ml | 5.0 | 7.5 | 9.0 | 9.9 | 9.94 | 9.98 | 10 | 10.04 | 10.18 | 11 | 12 |
| E , mV | 0.20 | 0.30 | 0.37 | 90 | 110 | 123 | 150 | 190 | 200 | 250 | 270 |
| V , ml | 13 | 14 | 14.9 | 14.93 | 14.97 | 15 | 15.1 | 15.2 | 15.5 | 16.0 | |
| E , mV | 290 | 310 | 350 | 370 | 400 | 440 | 500 | 520 | 550 | 560 | |

15. The potential changes for a silver-silver chloride electrode at chloride concentrations of 100, 150, and 200 $\mu\text{g/litre}$ were, respectively, 3.0, 4.2, and 5.8 mV.

Determine the concentration of chlorides if the change of the electrode potential is 6.2 mV.

SECTION B

16*. Calculate the potential of a copper electrode in a solution containing 24.2 g of a crystal hydrate of copper nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in 150 ml of the solution, relative to a 0.1*N* silver-silver chloride electrode at 20 °C.

17*. Calculate the potential of a zinc electrode in a solution containing 0.680 g of zinc chloride and 0.805 g of a crystal hydrate of zinc sulphate in a volume of 500 ml relative to a calomel electrode (0.1*N* NCE) at 20 °C.

18*. At 30° C the reading on a 100-cm potentiometric bridge for a Weston standard cell is equal to 52.8 cm, and the reading for a quinhydrone electrode relative to a calomel half-cell (0.1*N* NCE) is 12.35 cm.

Determine the pH of the solution.

19. The potential of a platinum electrode relative to a calomel half-cell (1*N* NCE) at 20 °C in a solution of a mixture of FeCl_3 and FeCl_2 is 0.215 V.

How much of a 0.05*N* solution of KIO_3 must be mixed with this solution for the potential to increase by 100 mV if the initial volume of a 0.2*N* solution of FeCl_2 in the mixture was 100 ml.

20*. How much of a 0.1*N* NaOH solution must be mixed with 100 ml of a 0.05*N* solution of nickel sulphate for the potential of the nickel electrode in this solution at 20 °C to be changed by 20 mV?

21*. On potentiometric titration with a similar solution (by the method of additions), to 50 ml of an HCl solution was added 2.5 ml of a 0.01*N* solution of HCl. The value of the potential of the quinhydrone electrode in this case increased from 200 to 259.1 mV at 25 °C.

Find the normality of the hydrochloric acid.

22. On potentiometric titration, to 20 ml of a sodium hydroxide solution was added 20 ml of 0.01*N* hydrochloric acid; the potential of the hydrogen electrode was found to be equal to 247 mV.

On subsequent addition of 0.8 ml of 0.01*N* hydrochloric acid the potential dropped to 228 mV.

Find the normality of the sodium hydroxide solution being analysed.

23*. Calculate the concentration of silver ions above the precipitate and the volume of the excess of a 0.1*N* potassium chloride solution if on titration of 100 ml of a 0.1*N* solution of silver nitrate the potential of the silver electrode relative to the hydrogen electrode became equal to 0.418 V at 20 °C. Ignore the change in the volume of the solution.

24*. Plot the curve for the titration of a chloride and iodide with a 0.1*N* solution of silver nitrate at 20 °C if the solution has been prepared from a sample weighing 5.6750 g and containing 50 per cent of chloride ions and 25 per cent of iodide ions. The initial volume of the solution is 50 ml.

25*. Construct a differential curve for the potentiometric titration of 50 ml of a 0.1*N* solution of $\text{Na}_2\text{S}_2\text{O}_3$ with a 0.1*N* solution of KBrO_3 at 20 °C.

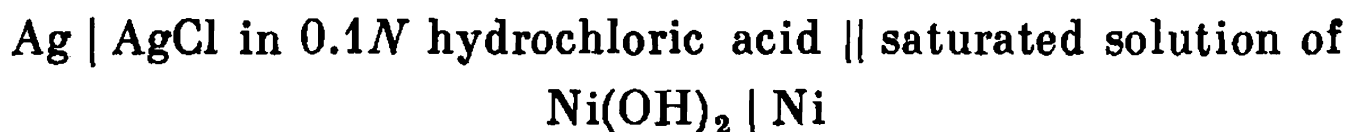
26. In a sample of steel weighing 2.5 g the chromium is oxidized to chromic acid and then titrated with a 0.103*N* solution of iron(II) sulphate.

Calculate the percentage content of chromium in the steel from the following titration results:

| | | | | | | | | |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| <i>V</i> , ml | 0 | 5 | 10 | 20 | 30 | 35 | 36 | 37 |
| <i>E</i> , V . . | 0.650 | 0.700 | 0.800 | 0.820 | 0.860 | 0.879 | 0.885 | 0.887 |

| | | | | | | | |
|-------------------|-------|-------|-------|-------|-------|-------|-------|
| <i>V</i> , ml . . | 37.5 | 38 | 38.3 | 38.4 | 39 | 43 | 45 |
| <i>E</i> , V . . | 0.887 | 0.885 | 0.884 | 0.505 | 0.495 | 0.480 | 0.470 |

27*. The emf of the cell



at 20° C is equal to 668 mV.

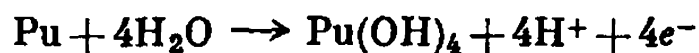
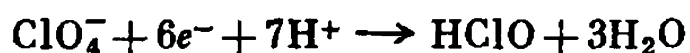
Determine the SP of nickel hydroxide.

28*. The potential of a quinhydrone electrode relative to a 0.1*N* calomel electrode in a 0.01*N* solution of arsenic acid is 27 mV.

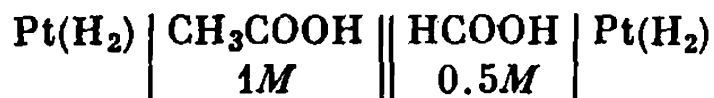
Determine the ionization constant of arsenic acid.

SECTION C

29*. Using the tables of electrode potentials, determine the standard electrode potentials of the following reactions:



30. Determine the emf of the following cell at 25 °C:



if the dissociation constant of acetic acid is 1.8×10^{-5} and that of formic acid, 1.27×10^{-3} .

31. In a potentiometric determination of a chloride ion the solution was titrated with a 0.01*N* solution of silver nitrate in a cell of 500-ml capacity with a silver electrode and a saturated calomel electrode used as the reference electrode. Near the equivalence point the value of emf on addition of 5 ml of titrant is 0.232 V, on addition of

5.5 ml it is 0.284 V, and when 6 ml is added the emf is 0.305 V.

Calculate the end point of titration and the quantity of the chloride ion in the solution being examined.

32. On pH-metric titration of a mixture of small amounts of NaOH and Na_2CO_3 with a 0.01N solution of HCl the following results were obtained:

| | | | | |
|--------------------------|-------|-------|-------|-------|
| Volume of 0.01N HCl, ml | 1.00 | 3.00 | 10.60 | 11.00 |
| pH of solution | 11.25 | 11.12 | 4.00 | 3.80 |

Calculate the content of NaOH and Na_2CO_3 in the mixture if it is known that the volume of the solution being titrated was 50 ml and the content of Na_2CO_3 in it did not exceed 5×10^{-5} g-eq/litre.

33. To 20 ml of a solution of sodium tetraborate was added 1 ml of a 0.01N hydrochloric acid and the volume of the resulting solution was made up to 50 ml with water. To an aliquot part of the solution ($\text{pH} \approx 5.4$), equal to 10 ml, was added first 0.2 ml and then 0.1 ml of a 0.01N hydrochloric acid. The values of the potentials of the quinhydrone electrode at 25 °C after the addition of hydrochloric acid were 220 and 230 mV, respectively.

Calculate the normality of the initial solution of sodium tetraborate.

34. Two beakers were filled each with 25 ml of a 0.1N solution of silver nitrate. The solutions were connected with a salt bridge containing potassium nitrate, and identical silver electrodes were introduced into them. To one of the beakers was added 25 ml of a solution of lead nitrate, as a result of which a potential difference of 13 mV developed between the electrodes.

Calculate the content of silver impurity in lead if the lead nitrate solution was prepared by dissolving 25 g of lead in nitric acid and by diluting the resulting solution to 250 ml.

35. From an air pipe one-hundredth of the volume of the flowing air is continuously drawn with the aid of a special divider, the air containing vapours of hydrogen chloride. The air is passed at a flow rate of 0.2 litre per minute through a measuring cell of 100-ml capacity with a hydrogen electrode

and a 0.1*N* calomel electrode and the emf is measured every 2 hours:

| | | | | | | | |
|--------------|-----|-----|-----|-----|-----|-----|-----|
| Time, hr . . | 0 | 2 | 4 | 6 | 8 | 10 | 12 |
| Emf, mV . . | 494 | 466 | 451 | 446 | 435 | 432 | 421 |

Determine the amount of hydrogen chloride flowing through the air line at each period of time and the total amount of hydrogen chloride in the air passed for 12 hours.

36*. A 100-ml volume of a 0.1*N* zinc chloride solution is titrated with a 0.1*N* solution of complexon III.

Determine the magnitude of the jump on the titration curve to within 0.01 per cent before and after the point of equivalence.

37*. The data obtained for the system quinhydrone electrode-saturated calomel electrode in a solution of an organic acid at 35 °C during the titration with sodium hydroxide are as follows: the emf before titration is 0.2872 V, after the titration of 50 per cent of the acid, 0.1771 V, after the titration of 99 per cent of the acid, 0.0519 V, after the titration of 99.9 per cent, -0.0061 V, and at the equivalence point, -0.0795 V.

Determine the mean value of the ionization constant of the acid and its degree of dissociation.

38*. A hydrogen electrode and a 0.1*N* calomel electrode are dipped into an absorbing vessel containing barium hydroxide, the emf of the system being 1.1060 V. Through the solution is passed the carbon dioxide produced by the acid decomposition of 2.35 g of a mineral containing calcium carbonate. As a result of this the emf of the system decreases by 4.8 mV.

Determine the content of calcium carbonate in the mineral if the temperature of the experiment is 30 °C.

39. When a solution of nitrogen-containing compounds was titrated potentiometrically with perchloric acid in the medium of ethyl methyl ketone, the following titration jumps were obtained on the titration curve: piperidine, 500 mV; methylbenzimidazole, 250 mV; 3,5-dimethylpyrazole, 100 mV; acrydine, 150 mV; pyridine, 120 mV.

What can be said about the strength of the given bases in methyl ethyl ketone? What will be the shape of the titra-

tion curve for a mixture of piperidine, methylbenzimidazole and 3,5-dimethylpyrazole titrated with perchloric acid?

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. Why cannot the pH of the solution be calculated from the emf when glass electrodes are used?

(a) Because the dependence of the potential of a glass electrode on pH is curvilinear.

(b) Because the potential of a glass electrode depends on the composition of the liquid inside the electrode.

(c) Because the potential of a glass electrode depends on the composition of the glass and its thickness and these factors are difficult to take into account.

(d) The pH of the solution can be calculated from the value of the glass electrode potential provided that the hydrogen electrode is used as the comparison electrode.

(e) Because the potential of the glass electrode depends not only on the pH of the solution but also on the concentration of other ions present in the solution.

2. Why are polarized electrodes used in potentiometric analysis?

(a) They are used to titrate systems that cannot be titrated with ordinary electrodes.

(b) They are used to titrate fast potentiometric systems.

(c) When these electrodes are used, separate titration jumps are obtained for mixtures of weak and strong acids and bases, for which the use of unpolarized electrodes gives a total titration jump.

(d) They are used to titrate very dilute oxidants and reductants when the titration curve obtained with ordinary electrodes shows no jump.

(e) They are used to titrate slow potentiometric systems.

3. Which of the graphs given in Fig. 57 reflects correctly the titration curve of a mixture of Ti^{2+} ($E_{\text{Ti}^{2+}/\text{Ti}^{3+}} = -0.37 \text{ V}$) and Cu^+ ($E_{\text{Cu}^+/\text{Cu}^{2+}} = +0.15 \text{ V}$), the titration being carried out with potassium permanganate?

4. What are the advantages and limitations of potentiometric titrations in nonaqueous media?

(a) In nonaqueous media, there can be titrated organic compounds that are insoluble in water, but it is difficult to choose indicator electrodes for them.

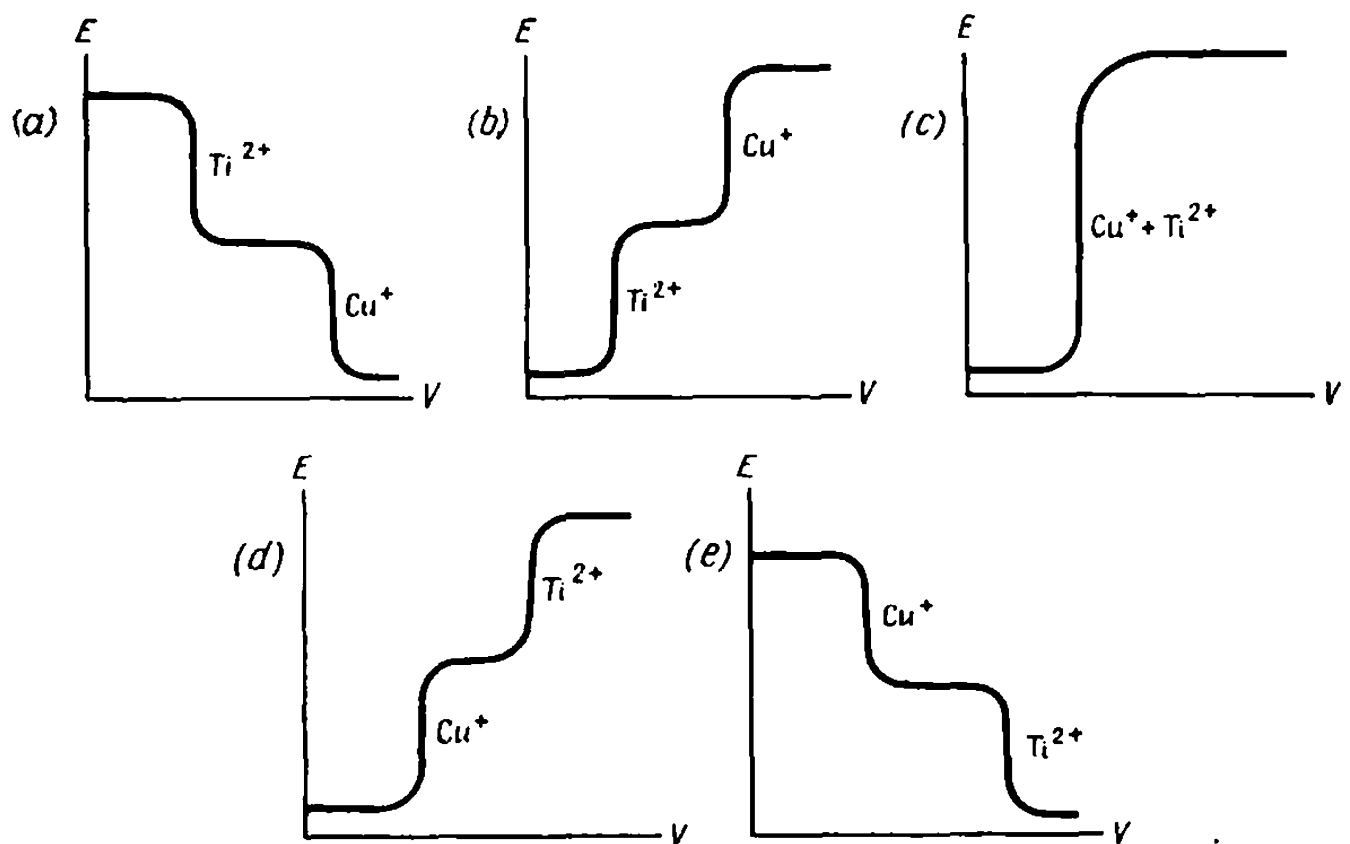


Figure 57

(b) In nonaqueous media, the titration proceeds faster than in aqueous solutions and very precise potentiometers are needed.

(c) In nonaqueous media, the potential of the glass electrode is very steady and the pH value can be calculated from the potential.

(d) In nonaqueous media, substances can be titrated that react with water; a disadvantage is that the electrical conductance of organic solvents is low.

(e) Mixtures of certain strong acids and bases can be titrated separately in nonaqueous media.

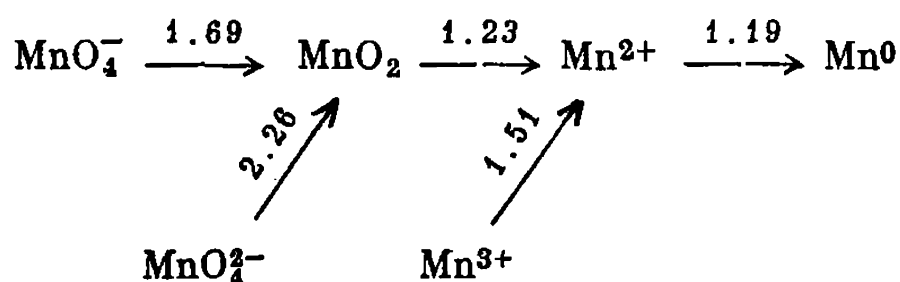
(f) Mixtures of oxidants can be titrated, which give a total jump in water.

(g) In nonaqueous media, there can be titrated mixtures of certain acids and bases that give a total jump in water. The difficulty with the titration in nonaqueous media lies in the complexity of creating a sufficiently conducting medium.

(h) In nonaqueous media, use may be made of indicator electrodes which are inapplicable in an aqueous medium.

(i) The titration in a nonaqueous medium does not offer special advantages and its complexity is that it requires more sensitive apparatus.

5. The scheme given below shows the electrode potentials of the transition of manganese from one valence to another:



Which of the answers given below are correct for the potentials of other electron transitions?

(a) $\text{Mn}^{3+} + 3e \rightarrow \text{Mn}^0$. $E = \frac{1.51 + 1.19 \times 2}{3} = 1.30$.

(b) $\text{MnO}_4^- + 4e + 8\text{H}^+ \rightarrow \text{Mn}^{3+} + 4\text{H}_2\text{O}$. $E = \frac{1.69 + 1.23 - 1.51}{4} = 0.37$.

(c) $\text{MnO}_2 + e + 4\text{H}^+ \rightarrow \text{Mn}^{3+} + 2\text{H}_2\text{O}$. $E = \frac{1.23 \times 2 - 1.51}{1} = 0.95$.

(d) $\text{MnO}_4^{2-} + 4e + 8\text{H}^+ \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$. $E = \frac{2.26 \times 2 + 1.23 \times 2}{4} = 1.74$.

(e) $\text{Mn}^{3+} + 3e \rightarrow \text{Mn}^0$. $E = \frac{1.51 + 1.19}{3} = 0.90$.

(f) $\text{MnO}_4^- + e \rightarrow \text{MnO}_4^{2-}$. $E = \frac{2.26 - 1.69}{1} = 0.57$.

(g) $\text{MnO}_4^{2-} + 3e + 8\text{H}^+ \rightarrow \text{Mn}^{3+} + 4\text{H}_2\text{O}$. $E = \frac{2.26 + 1.23 - 1.51}{3} = 0.66$.

(h) $\text{MnO}_2 + 4e + 4\text{H}^+ \rightarrow \text{Mn}^0 + 2\text{H}_2\text{O}$. $E = \frac{1.23 \times 2 + 1.19 \times 2}{4} = 1.21$.

6. Which of the formulas given under B should be used to determine the hydrogen electrode potential for the conditions indicated under A?

A

(a) At the equivalence point, on titration of a weak acid with a strong base.

(b) On titration of 50 per cent of a strong acid with a strong base.

(c) At the equivalence point, on titration of a strong acid with a strong base.

(d) On titration of a strong acid with a strong base when 90 per cent of the acid has been titrated.

(e) On titration of a weak base with a strong acid when 99 per cent of the base has been titrated.

(f) At the equivalence point, on titration of a weak acid with a strong base.

(g) On titration of a weak acid with a strong base when 50 per cent of the acid has been titrated.

(h) On titration of a weak acid with a strong base when 90 per cent of the acid has been titrated.

B

$$(1) \quad E = +0.058 \log \frac{C_{\text{acid}}}{10}.$$

$$(2) \quad E = -0.058 (14 - \text{pK}_{\text{base}} - \log 99).$$

$$(3) \quad E = +0.058 \log 10 C_{\text{acid}}.$$

$$(4) \quad E = -0.058 \text{pK}_{\text{acid}}.$$

$$(5) \quad E = +0.058 \log C_{\text{acid}}/2.$$

$$(6) \quad E = -0.058 (7 + 0.5 \text{pK}_{\text{acid}} - 0.5 \text{pK}_{\text{base}}).$$

$$(7) \quad E = -0.058 (\text{pK}_{\text{acid}} + \log 9).$$

$$(8) \quad E = -0.058 \times 7 = -0.406.$$

$$(9) \quad E = -0.058 (7 + 0.5 \text{pK}_{\text{acid}} + 0.5 \text{pK}_{\text{base}}).$$

$$(10) \quad E = -0.058 (7 + 0.5 \text{pK}_{\text{acid}} + 0.5 \log C_{\text{acid}}).$$

7. Indicate the curves shown in Fig. 58 that correspond to the potentiometric titrations listed below. The cross on the potential axis stands for the potential -0.410 V corresponding to the neutral solution ($\text{pH} = 7$).

(a) Titration of a strong acid with a weak base.

(b) Titration of an oxidant with a reductant if the difference $E_{\text{ox}} - E_{\text{red}}$ is not great.

(c) Titration of a weak base with a strong acid.

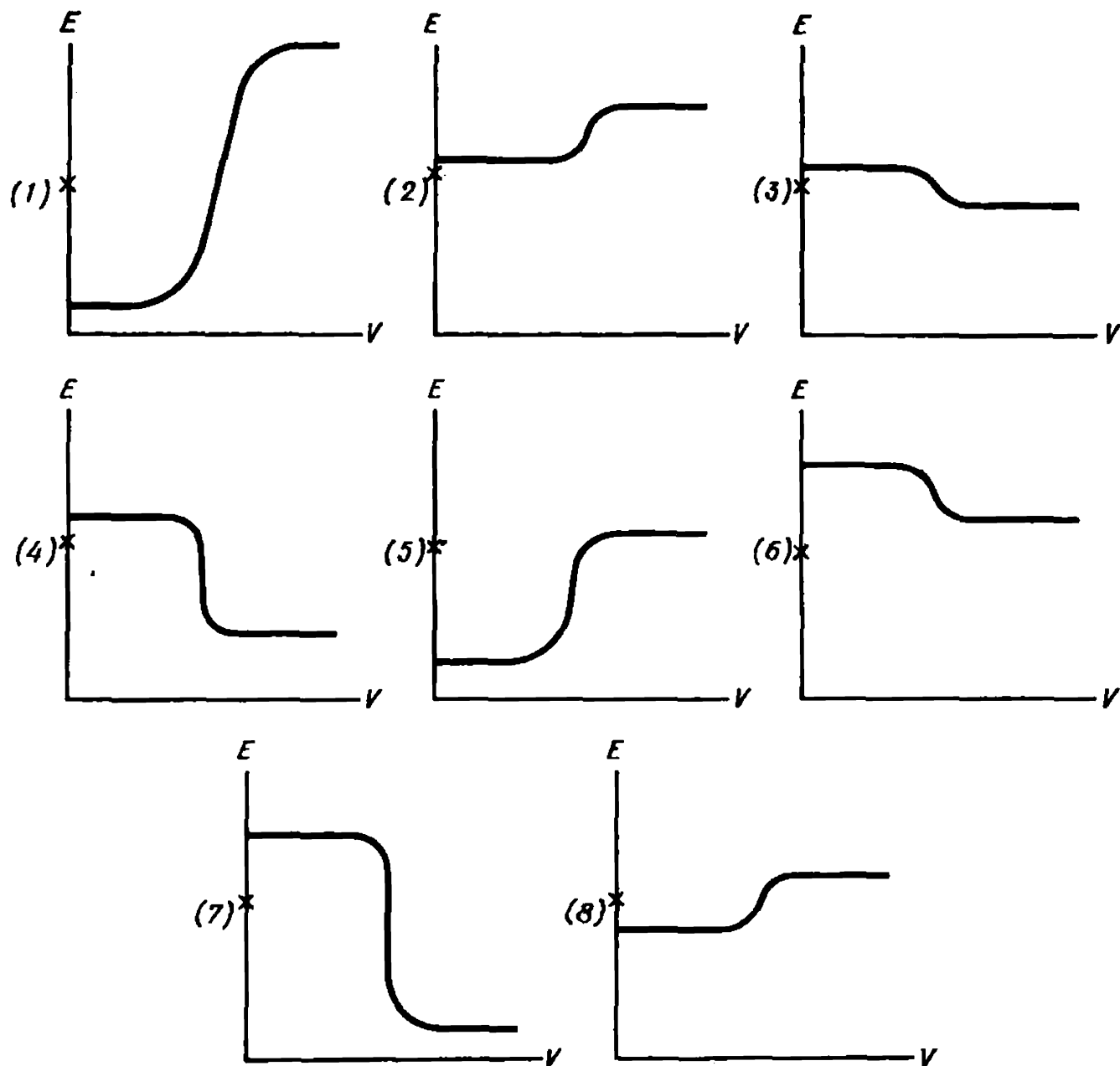


Figure 58

(d) Titration of a reductant with an oxidant if the difference $E_{\text{ox}} - E_{\text{red}}$ is not great.

(e) Titration of a weak acid with a weak base.

(f) Titration of a strong acid with a strong base.

(g) Titration of a reductant with an oxidant if the difference $E_{\text{ox}} - E_{\text{red}}$ is great.

(h) Titration of a weak base with a weak acid.

8. Using the handbook, find under B the potentials of the oxidation-reduction reactions indicated under A.

| A | B |
|--|---------------|
| (a) $\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e \rightarrow \text{Cr}(\text{OH})_3 + 5\text{OH}^-$ | (1) -0.96 . |
| (b) $\text{NiO}_2 + 4\text{H}^+ + 2e \rightarrow \text{Ni}^{2+} + \text{H}_2\text{O}$ | (2) $+1.75$. |
| (c) $\text{Au}_2\text{O}_3 + 6\text{H}^+ + 6e \rightarrow 2\text{Au} + 3\text{H}_2\text{O}$ | (3) $+1.23$. |
| (d) $\text{CNO}^- + \text{H}_2\text{O} + 2e \rightarrow \text{CN}^- + 2\text{OH}^-$ | (4) $+0.88$. |
| (e) $\text{AlO}_2^- + 2\text{H}_2\text{O} + 3e \rightarrow \text{Al} + 4\text{OH}^-$ | (5) -0.12 . |
| (f) $\text{N}_2\text{O}_4 + 2e \rightarrow 2\text{NO}_2^-$ | (6) -0.71 . |
| (g) $\text{AsO}_4^{3-} + 2\text{H}_2\text{O} + 2e \rightarrow \text{AsO}_2^- + 4\text{OH}^-$ | (7) -2.35 . |
| (h) $\text{ClO}_3^- + 3\text{H}^+ + 2e \rightarrow \text{HClO}_2 + \text{H}_2\text{O}$ | (8) $+1.42$. |

9. In the potentiometric titration of a mixture of potassium iodide and chloride with silver nitrate, using silver and calomel electrodes, to the solution there was accidentally added an excess of ammonia. Find in Fig. 59 the

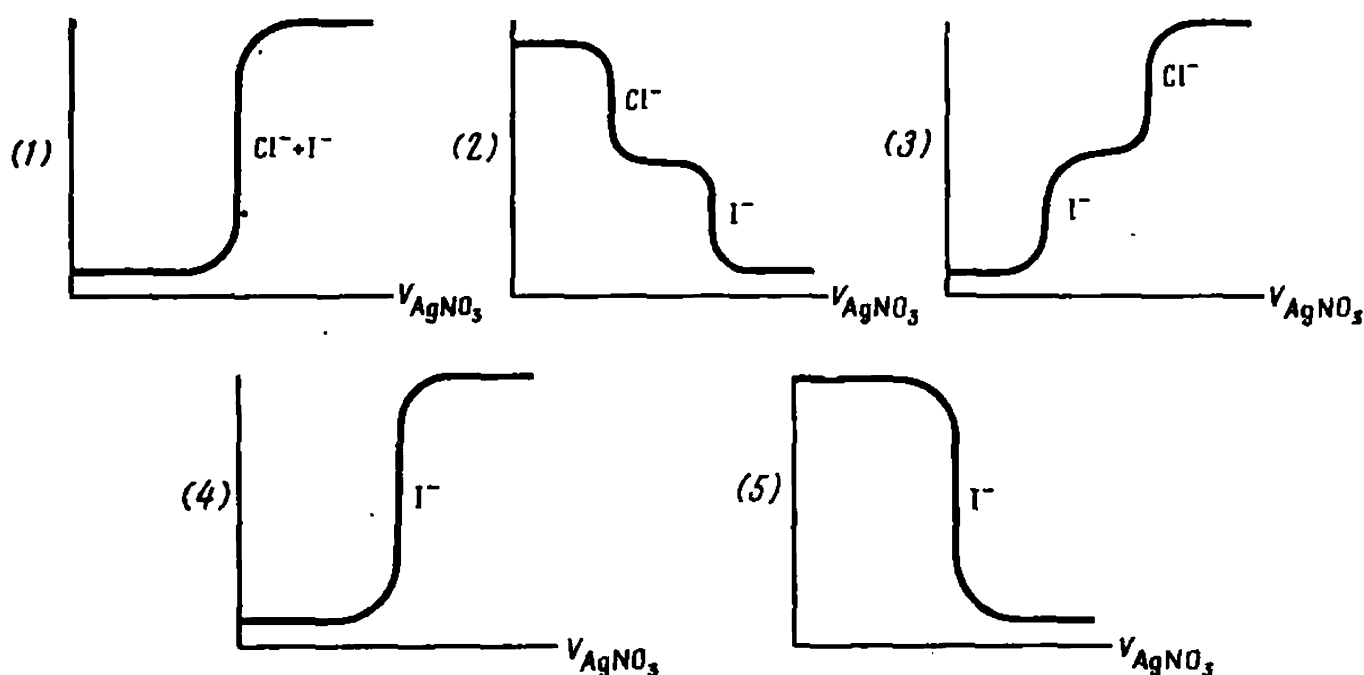


Figure 59

titration curve that was obtained under the conditions specified, and indicate below the cause responsible for the appearance of a distorted curve and the ways for obtaining the normal titration curve.

(a) Silver chloride is soluble in an ammoniacal solution and chloride ions cannot be titrated. To obtain accurate results ammonia must be removed by boiling.

(b) Silver chloride and iodide are soluble in an ammoniacal solution and one jump will therefore be obtained on the

titration curve. To obtain correct results, ammonia must be neutralized with hydrochloric acid.

(c) Owing to the solubility of precipitates in ammonia there will be two jumps on the titration curve, but their sequence will be changed, the first jump being for chlorine and the second for iodine. Ammonia does not interfere with the titration.

(d) In the presence of ammonia the electrode potential will fall rather than increase during the titration, but there will be two jumps on the titration curve. Titration may be carried out in the presence of ammonia.

(e) Chloride ions will not be titrated because of the solubility of silver chloride in ammonia. It is only the character of the titration curve of the iodide ion that will change in ammoniacal solution, and the potential will fall rather than increase.

10. Find under A the correct cause responsible for the appearance of the asymmetry potential of the glass electrode, and under B the ways of reducing it.

A

(a) The asymmetry potential arises from the difference in the ionic strength of the solutions inside the electrode and outside it.

(b) The asymmetry potential arises from the difference in the pH of the solutions inside and outside the electrode.

(c) The asymmetry potential arises from the difference in the properties of the external and internal surfaces of the electrode.

(d) The asymmetry potential results from the difference in the composition of the glass on the external and internal surfaces of the electrode and in the composition of the solutions inside and outside the electrode.

(e) The asymmetry potential develops as a result of the prolonged contact of the external electrode surface with solutions of different composition and different acidity.

B

(1) The asymmetry potential is eliminated by the prolonged boiling of the electrode.

(2) The asymmetry potential cannot be eliminated but it can be taken into account when calibrating the electrode.

(3) The asymmetry potential can be eliminated by allowing the electrode to stand in water for a long time.

(4) The asymmetry potential can be eliminated by allowing the electrode to stand in a strong acid for a prolonged time.

(5) The asymmetry potential cannot be eliminated but it can be reduced by keeping the electrode in a strong alkali.

Polarography

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. Determine the characteristic of a capillary at a potential of -0.6 V relative to the bottom mercury (mercury pool) if 100 drops of mercury weigh 990 mg and the time of formation (drop time) of 10 drops is 45 sec.

Solution:

$$K = m^{2/3} \tau^{1/6} \quad m = \frac{990 \times 10}{100 \times 45} = 2.2 \text{ mg/sec}$$

$$K = 2.2^{2/3} \times 4.5^{1/6} = 1.692 \times 1.285 = 2.174$$

Example 2. Determine the value of the limiting diffusion current of zinc if $C = 3 \times 10^{-3}$ mole/litre, $D = 0.72 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$, $m = 3 \text{ mg/sec}$, $\tau = 4 \text{ sec}$.

Solution: Substituting the data given into the Ilkovic equation, we obtain:

$$i_d = 605 \times 2 \times 3 \times 3^{2/3} \times 4^{1/6} \sqrt{0.72 \times 10^{-5}} = 25.4 \mu\text{A}$$

Example 3. A 0.2-g sample of steel containing copper was dissolved in nitric acid and the volume of the resulting solution was made up to 50 ml with water. When 5 ml of the solution was analysed polarographically in 20 ml of the background solution, the height of the copper wave was 37 scale divisions.

Calculate the percentage content of copper in steel if it is known that when a solution of $3 \times 10^{-5} \text{ g}$ of copper in 25 ml is analysed polarographically, the wave height is 30 divisions.

Solution: If the height of the copper wave is 37 divisions on the recorder scale of the polarograph, the amount of

copper will be

$$\begin{array}{rcl} 3 \times 10^{-5} \text{ g} & = & 30 \text{ scale divisions} \\ x \text{ g} & = & 37 \text{ scale divisions} \\ \hline x & = & 3.7 \times 10^{-5} \text{ g} \end{array}$$

Since 5 ml of a solution are taken from 50 ml to run a polarogram, the content of copper in steel is

$$3.7 \times 10^{-5} \times 10 = 3.7 \times 10^{-4} \text{ g}$$

or

$$\frac{3.7 \times 10^{-4} \times 100}{0.2} = 0.18 \text{ per cent}$$

Example 4. When running a polarogram of solutions of copper-containing standard steel samples the following results were obtained:

| | | | | | |
|-----------------------------|-----|------|------|------|------|
| Sample No. | 1 | 2 | 3 | 4 | 5 |
| Copper content, % | 0.1 | 0.19 | 0.32 | 0.41 | 0.54 |
| Wave height, mm | 6 | 12 | 20 | 26 | 35 |

Plot the calibration curve and calculate the percentage of copper in the unknown sample if the height of the polarographic wave is 15 mm.

Solution: We plot a graph of the wave height against the copper content (see Fig. 60). From the graph we find that

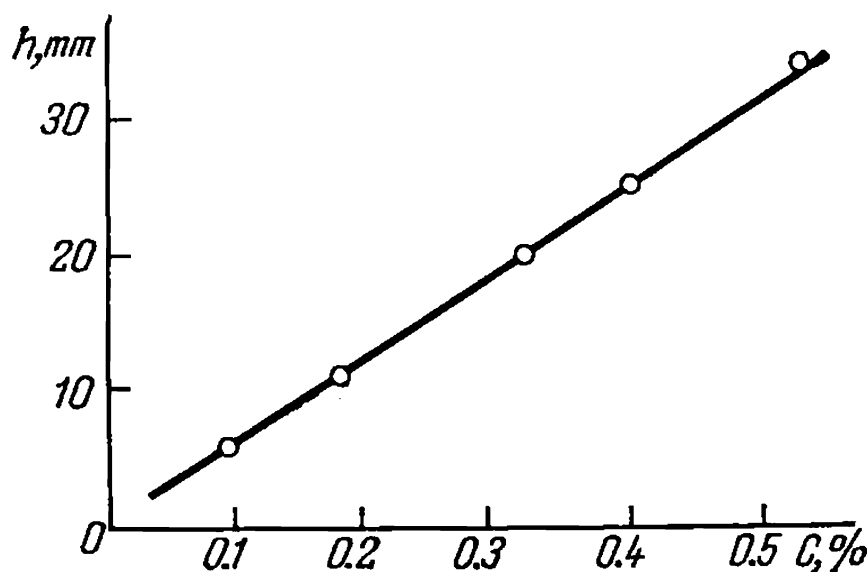


Figure 60

the wave height 15 mm corresponds to a copper content of 0.23 per cent.

Example 5. Calculate the concentration of cadmium in a solution if on analysis of 15 ml of a solution containing Cd^{2+} ions by the method of standard additions the height of the polarographic wave of cadmium was 20.5 mm. After adding 2 ml of a standard solution—0.053*N* solution of cadmium chloride—the wave height increased to 24.3 mm.

Solution: We use the equation

$$C_x = \frac{C_{st}}{\frac{i'}{i_x} \cdot \frac{V_{st} + V_x}{V_{st}} - \frac{V_x}{V_{st}}} = \frac{0.053}{\frac{24.3}{20.5} \times \frac{2+15}{2} - \frac{15}{2}} = 0.02N$$

Example 6. In the amperometric titration of acetaldehyde with 2,4-dinitrophenylhydrazine at a potential of -1.4 V with respect to the mercury anode (mercury pool) the following results were obtained:

| | | | | | | | | |
|--|-----|------|------|------|------|------|------|-----|
| Volume of 2,4-dinitrophenylhydrazine, ml | 0.2 | 0.25 | 0.35 | 0.45 | 0.53 | 0.61 | 0.69 | 0.9 |
| Current, μA | 0 | 78 | 63 | 45 | 30 | 30 | 39 | 60 |

Find the equivalence point and the content of acetaldehyde in the polarographic cell if the titre of 2,4-dinitro-

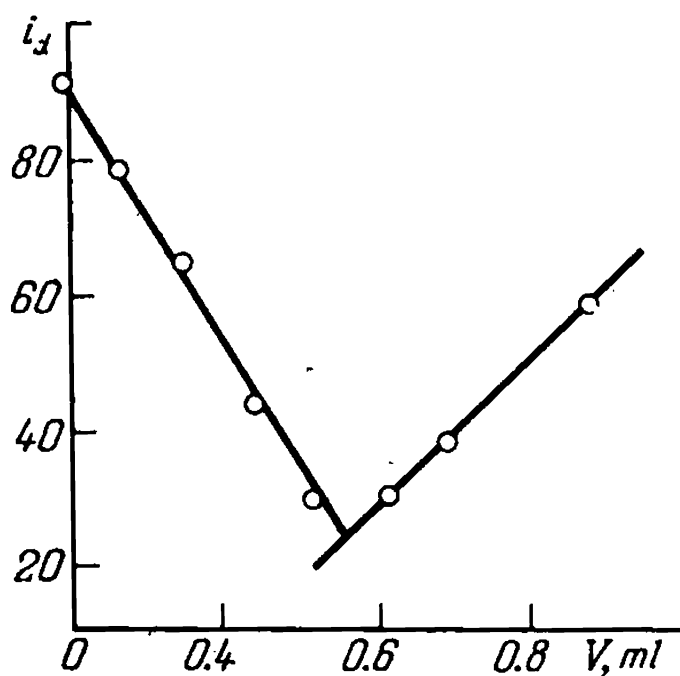


Figure 61

phenylhydrazine with respect to acetaldehyde is equal to 5.6×10^{-8} g/ml.

Solution: From the plot of i_d vs. V in Fig. 61 it is seen that the equivalence point corresponds to the 0.55-ml

volume of 2,4-dinitrophenylhydrazine. On this basis one can calculate the content of acetaldehyde in the solution being analysed from the formula

$$C = VT = 0.55 \times 5.6 \times 10^{-6} \text{ g}$$

Example 7. When running a polarogram of 5 ml of a saturated solution of lead bromide against the ammonium-ammonia background the height of the lead wave was found to be 26 mm. The wave height obtained when running a polarogram of a 0.01M standard solution of lead under the same conditions was 20 mm.

Determine the solubility product of lead bromide.

Solution: We make up the proportion:

| | |
|-------------------------------|-------|
| 0.01M lead solution | 20 mm |
| x | 26 mm |

$$x = 1.3 \times 10^{-2} \text{ g-ion/litre}$$

$$\text{SP} = 4x^3 = 9.1 \times 10^{-6}$$

Example 8. Using the polarographic data for thallium against the background of complexon III, determine the

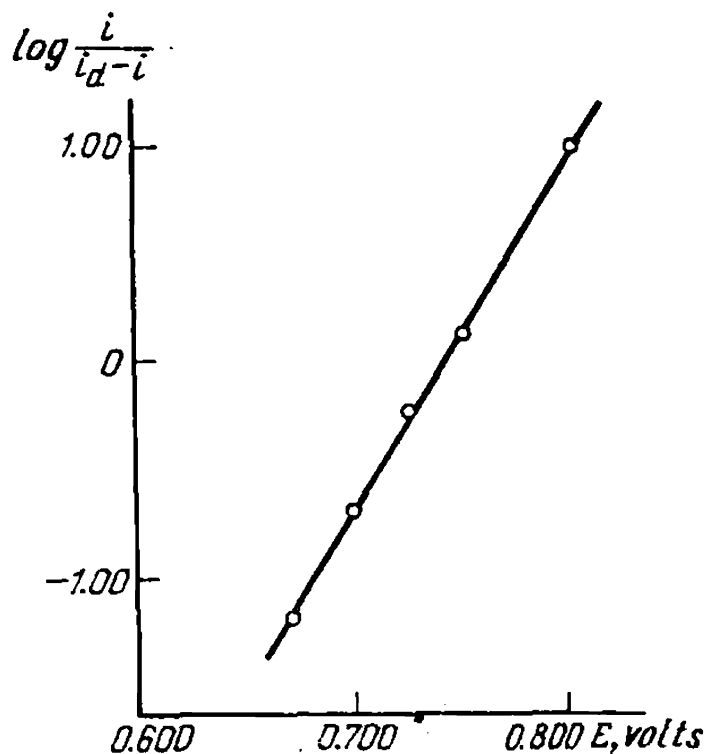


Figure 62

half-wave potential and the number of electrons taking part in the reaction:

| | | | | | | | | | |
|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Potential, V | 0.500 | 0.650 | 0.675 | 0.700 | 0.725 | 0.750 | 0.775 | 0.800 | 0.900 |
| Current, μ A | 0 | 1.1 | 3.6 | 6.9 | 15.0 | 26.8 | 35.8 | 41.0 | 45 |

Solution: From the data given we determine $\log [i/(i_d - i)]$ and construct a plot of E versus $\log [i/(i_d - i)]$, assuming i_d to be equal to 45.

| | | | | | | | |
|--------------------------|-------|-------|-------|-------|-------|-------|-------|
| E, V | 0.650 | 0.675 | 0.700 | 0.725 | 0.750 | 0.775 | 0.800 |
| $\frac{i}{i_d - i}$ | 0.025 | 0.087 | 0.18 | 0.50 | 1.45 | 3.9 | 10.2 |
| $\log \frac{i}{i_d - i}$ | -1.60 | -1.16 | -0.74 | -0.30 | 0.16 | 0.59 | 1.02 |

From the graph shown in Fig. 62 we determine $E_{1/2} = 0.74V$ and the cotangent of the slope from the limiting readings:

$$\frac{0.800 - 0.650}{1.02 - (-1.60)} = \frac{0.150}{2.62} = 0.057$$

Hence the electrode process involves only one electron.

2. MULTIVARIANT PROBLEMS

1. Calculate the value of diffusion limiting current for the ions indicated (see Table 41) from the data given in the table.

TABLE 41

| Vari- ant | Ion | Mass of 100 drops, mg | Time of for- mation of 25 drops, seconds | Diffusion coefficient, $D \times 10^5$, $\text{cm}^2 \cdot \text{sec}^{-1}$ | Concentration |
|--------------|------------------|-----------------------------|---|---|----------------------|
| I | Cd^{2+} | 200 | 75 | 0.72 | $2 \times 10^{-3} M$ |
| II | Pb^{2+} | 215 | 102 | 0.98 | 0.005 g/ml |
| III | Cu^{2+} | 300 | 100 | 1.98 | 0.0020N |
| IV | Ti^{2+} | 260 | 112.5 | 2.00 | 0.250 g/l |
| V | Zn^{2+} | 310 | 112.5 | 0.72 | $3 \times 10^{-4} M$ |
| VI | Zn^{2+} | 280 | 120 | 0.69 | 0.0065 g/ml |
| VII | Cu^{2+} | 210 | 75 | 1.98 | 0.001N |
| VIII | Cd^{2+} | 285 | 95 | 0.72 | 0.002M |

2. To plot a calibration graph in the determination of cadmium use was made of a $10^{-4}N$ solution of a cadmium salt, whose aliquot parts were diluted with a 0.1N ammo-

nium-ammonia solution to 25 ml and analysed polarographically. The data obtained were as follows:

| | | | | | | |
|----------|---|----|------|----|----|----|
| V , ml | 1 | 2 | 3 | 4 | 5 | 6 |
| h , mm | 9 | 16 | 26.5 | 35 | 41 | 54 |

Different samples of alloys containing cadmium were dissolved in nitric acid and diluted, after treatment, to the volumes indicated below. When running a polarogram of 5 ml of solutions under the same conditions the following data were obtained:

| | | | | | | | | |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|
| Variant | I | II | III | IV | V | VI | VII | VIII |
| g , g | 0.100 | 0.250 | 0.500 | 1.000 | 0.200 | 0.250 | 0.500 | 0.750 |
| V , ml | 50 | 50 | 100 | 250 | 50 | 25 | 100 | 100 |
| h , mm | 18 | 22 | 21 | 25 | 10 | 17 | 32 | 41.5 |
| | 17.5 | 22 | 23 | 22.5 | 12 | 19 | 33 | 42.0 |
| | 16 | 24 | 23.5 | 26.5 | 10.5 | 18 | 33 | 43.0 |

Calculate the average content of cadmium in the alloys and the error of the determination.

3. Calculate the concentration of copper (in moles per litre) in a solution if on analysis of V ml of the unknown solution by the method of additions the wave h mm was obtained, and after the addition of W ml of a standard solution of concentration C the wave height increased to H mm:

| | | | | |
|----------|-------------|------------------------|-------------|-------|
| Variant | I | II | III | IV |
| V , ml | 10 | 25 | 25 | 50 |
| h , mm | 20.5 | 22 | 30 | 28.5 |
| W , ml | 2 | 4 | 3 | 2.5 |
| C | 0.05 mole/l | 2×10^{-4} g/l | 0.08 mole/l | 0.07N |
| H , mm | 24 | 26.5 | 35 | 35 |

| | | | | |
|----------|------------------------|-------|---------------------------|-------------|
| Variant | V | VI | VII | VIII |
| V , ml | 10 | 25 | 10 | 50 |
| h , mm | 26.5 | 18 | 20 | 12.5 |
| W , ml | 0.5 | 3 | 0.2 | 2.5 |
| C | 1×10^{-4} g/l | 0.12N | 1.5×10^{-4} g/ml | 0.02 mole/l |
| H , mm | 36 | 24 | 22 | 26 |

4. To reduce the sensitivity of a galvanometer, it was connected in series with resistance R_1 and in parallel with resistance R_2 . Calculate these resistances for the sensitivities indicated below if the galvanometer resistance $R_g = 550$ ohms, and its critical resistance is $R_{cr} = 7600$ ohms:

| | | | | | | | | |
|-------------|-----|-----|------|------|-------|-------|--------|--------|
| Variant | I | II | III | IV | V | VI | VII | VIII |
| Sensitivity | 1/2 | 1/5 | 1/20 | 1/50 | 1/100 | 1/500 | 1/1000 | 1/2000 |

5. In the polarographic analysis of V ml of a standard solution of a zinc salt with a zinc concentration of $0.5 \mu\text{g/ml}$ (sensitivity = $1/50$) a wave having a height of h cm was obtained.

What sensitivity approximately must be set on the instrument for the full scale 10 cm in length to correspond to the concentration C if:

| | | | | |
|--------------------|----------------------|-----------------------------------|--------------------------|--------------------|
| Variant | I | II | III | IV |
| V , ml | 1 | 2 | 2.5 | 3 |
| h , cm | 3 | 3 | 0.5 | 5 |
| C | $0.2 \mu\text{g/ml}$ | 0.05 g/l | 10^{-5} mole/l | $5 \mu\text{g/ml}$ |
| Variant | V | VI | VII | VIII |
| V , ml | 3.5 | 2.2 | 1.8 | 2 |
| h , cm | 1 | 7 | 9 | 5 |
| C | 10 mg/l | $5 \times 10^{-4} \text{ mole/l}$ | 100 mg/l | $1 \mu\text{g/ml}$ |

3. PROBLEMS

SECTION A

1. Determine the characteristic of a capillary at a potential of -0.6 V versus the mercury pool if 20 drops of mercury weigh 0.1760 g and the drop time is 88 seconds.

2. Determine the concentration of cadmium in a solution if $D = 0.72 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$, $m = 2.0 \text{ mg/sec}$, $\tau = 4.4 \text{ sec}$ and the current is $10 \mu\text{A}$.

3. Determine the current that flows through a polarographic cell at a potential of -1.0 V relative to the bottom mercury if the characteristic of the capillary is 1.92, the concentration of cadmium in the solution, $2 \times 10^{-3} \text{ g-ion/litre}$ and $D = 0.72 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$.

4. A 0.1-g sample of steel containing copper was dissolved in acid and after appropriate treatment the volume of the solution was made up to 25 ml with water and 5 ml of the background solution was diluted to 25 ml . When running a polarogram the height of the copper wave was found to be equal to 37.5 mm .

Calculate the percentage content of copper in the sample if in running a polarogram of 0.5 ml of a standard solution, containing copper and having a titre of 0.000064 g/ml , in 25 ml of the background a wave was obtained, which had a height of 30.0 mm .

5. A portion of waste water (50 ml) containing phenol was diluted to 250 ml and analysed polarographically. The height of the phenol wave at a sensitivity of 1/10 was found to be equal to 24.5 mm.

Determine the concentration of phenol in the waste water (in mg/litre) if in running a polarogram of a standard phenol solution containing 25.6 mg of phenol in 250 ml the wave height was found to equal 38.5 mm at a sensitivity of 1/100.

6. When running a polarogram of 15 ml of a solution of a zinc salt the height of the zinc wave was 29.5 mm. After the addition of 2 ml of a standard solution with a zinc concentration of 0.000256 g-ion/litre the wave height increased to 41.5 mm.

Determine the concentration of zinc in the solution being analysed (in moles per litre).

7. A 0.5650-g sample of a mineral containing titanium was dissolved and after appropriate treatment the solution was diluted with water to 200 ml. When running a polarogram of 10 ml of the solution containing Ti^{IV} the limiting current was found to be equal to 5.50 μA . After the addition of 0.25 ml of a solution of TiCl_4 having a concentration of 3.5×10^{-5} g/ml the magnitude of the limiting current increased to 6.35 μA .

Determine the percentage of TiO_2 in the mineral.

8. To plot a calibration graph in determining zinc equal amounts of a 0.045N solution of zinc chloride were transferred into 50-ml measuring flasks. The solutions were treated, diluted with water to the mark and then analysed polarographically. The following results were obtained:

| | | | | | | | | |
|--------------------------------------|---|----|----|----|----|----|----|----|
| Volume of zinc chloride solution, ml | 2 | 4 | 6 | 8 | 12 | 16 | 20 | 24 |
| Wave height, mm | 7 | 13 | 18 | 25 | 37 | 42 | 56 | 63 |

Plot the calibration graph and find the content of zinc, in grams, to which the wave heights 31, 17, and 51 mm correspond.

9. To plot a calibration graph in determining indium in semiconducting gallium, standard solutions were prepared and the limiting current was measured (the sensitivity of the instrument was 1/25):

| | | | | |
|--|-----|-----|-----|------|
| Concentration of indium, $\mu\text{g}/10$ ml | 0.2 | 0.4 | 0.6 | 1.0 |
| Limiting current, μA | 2.3 | 4.8 | 6.3 | 11.4 |

A 0.2-g sample of gallium was dissolved and after appropriate treatment the solution was diluted with water to 25 ml. With the sensitivity of the instrument being $1/10$, the value of the limiting current was found to be $8.5 \mu\text{A}$.

Determine the percentage content of indium in the gallium.

10. A 0.5-g sample of a mineral containing titanium, iron, and niobium (columbium) was dissolved in acid and the

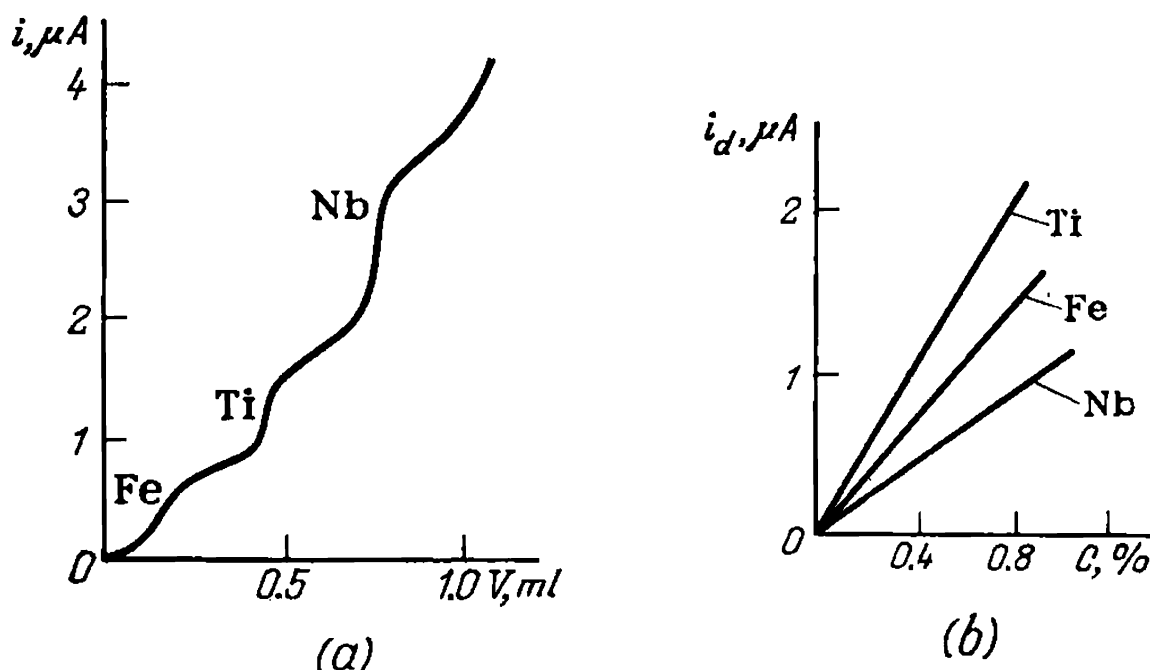


Figure 63

resulting solution was diluted to 100 ml with pyrophosphoric acid. When this solution was analysed polarographically, a polarogram was obtained, which is shown in Fig. 63a.

Determine the content of the indicated metals in the mineral by using the calibration graph shown in Fig. 63b.

11. Figure 64a shows the polarograms of gallium against the potassium chloride background in the presence of pyrocatechin (the numbers on the curves signify the concentration of Ga in mmoles per litre).

In the determination of gallium impurity in pure aluminium, 25 ml of a solution was prepared by dissolving a 0.15-g sample in acid and treating it appropriately. When the solution was analysed polarographically, the polarographic wave shown in Fig. 64b was obtained.

Determine the content of gallium in the aluminium.

12. Alpha-benzoinoxime (cupron) is a precipitating agent for copper in an ammonium-ammonia solution. In the same

solution at $\text{pH} = 9$ cupron is reduced at a dropping-mercury cathode, giving a polarographic wave with $E_{1/2} = -1.63$ volts vs. SCE. In the same conditions copper forms two waves with half-wave potentials of -0.1 and -0.5 volt, respectively.

Sketch the probable curves for the amperometric titration of copper by cupron at applied potentials of -0.35 , -1.0 ,

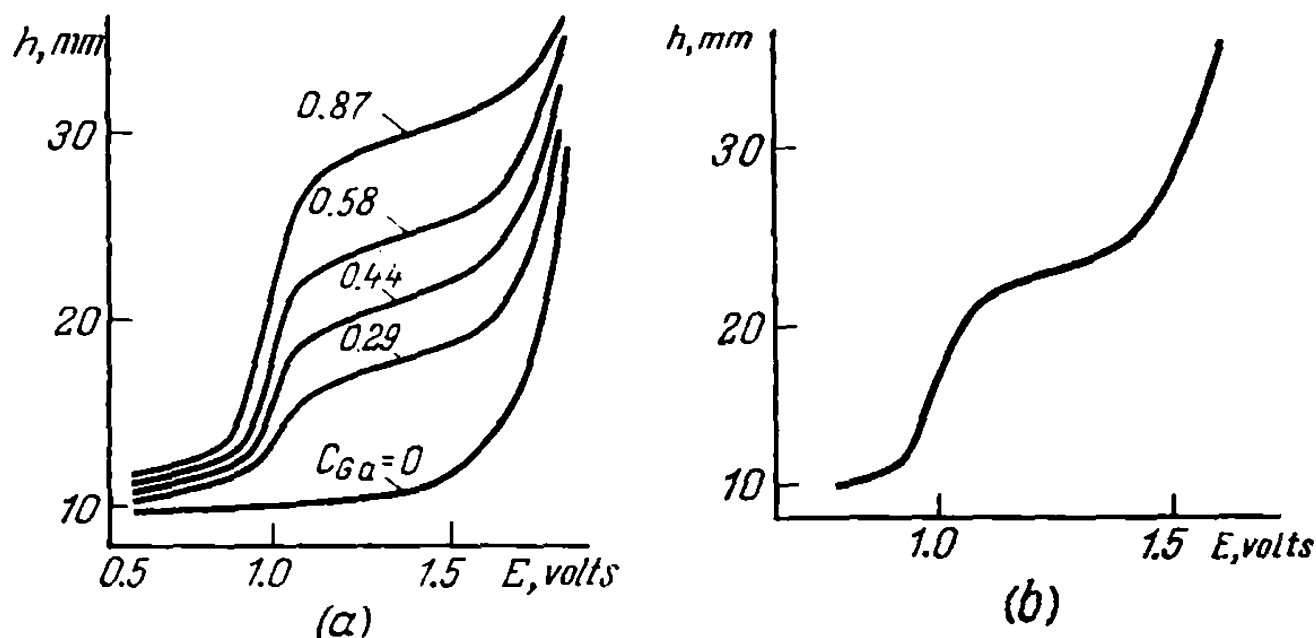


Figure 64

and -1.8 V. Which potential should be preferred for titration of copper in the absence of interfering cations? Which should be preferred in the presence of zinc if $E_{1/2}$ for zinc under the same conditions is -1.50 V?

13. To determine aluminium in a solution, use was made of the method of amperometric titration with a $0.01N$ solution of potassium fluoride; as a result, the ion AlF_6^{3-} was formed. The following wave heights were obtained for iron used as indicator:

| | | | | | | | | |
|----------|-----|-----|-----|------|-----|------|-----|------|
| V , ml | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 |
| h , mm | 45 | 45 | 44 | 44.5 | 44 | 44.5 | 44 | 43.5 |
| V , ml | 4.0 | 4.5 | 5.0 | 5.5 | 6.0 | 6.5 | 7.0 | 7.5 |
| h , mm | 43 | 43 | 42 | 40 | 20 | 10 | 8 | 7 |

Determine the percentage content of aluminium in the solution from the first inflection on the titration curves.

14. In the determination of indium by the method of amalgam polarography in a solution with a concentration

of indium of 3.5×10^{-8} mole per litre at a potential of -0.80 V the height of the indium peak was 26 mm for the time of accumulation 10 min.

To determine indium impurity in a semiconducting alloy, a 0.2-g sample of the alloy was dissolved in 100 ml of acid. Under the same conditions the indium peak was found to be small. After the time of accumulation was increased to 35 min the peak became equal to 11 mm.

Determine the percentage content of indium in the alloy.

15. The following data were obtained when taking a current-voltage curve for cadmium, a dropping-mercury electrode and an ammonium-ammonia background being used for the purpose:

| | | | | | | | | | |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $-E, V$ | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 1.0 |
| $h, \text{ mm}$ | 2 | 2 | 3 | 3.5 | 4.5 | 25 | 45 | 46 | 47 |

Calculate the half-wave potential of cadmium and the number of electrons taking part in the reaction.

16. Determine the characteristic of a capillary if at a potential of -1.5 V with respect to the mercury pool there are formed 19 drops of mercury for 1 minute, their total mass being equal to 120 mg.

17. At a potential of -0.8 V vs. SCE, to a solution of $5 \times 10^{-3} M$ for cadmium chloride and $0.1M$ for potassium chloride there corresponds a diffusion current of $50 \mu A$. The mercury flows out at a rate of 18 drops per 1 min and the mass of 10 drops of mercury is 0.0382 g.

Calculate the diffusion coefficient. What will be the current if the given capillary is replaced by another one, for which the drop time is 3.0 sec and the weight of 10 drops is 0.0420g?

18. A 0.1-g sample of metallic zinc containing cadmium impurity is dissolved in 50 ml of 6*N* hydrochloric acid and the solution is diluted with water to 250 ml. A 25-ml volume of the solution obtained is transferred into an electrolytic cell and an a-c polarogram is taken in the range of (-0.3) to (-1.0) V with respect to the bottom mercury. At a potential of -0.65 V the height of the cadmium peak is 60 mm. To this solution is added 5 ml of a $0.00005N$ cadmium chloride solution, following which the height of the cadmium peak increases to 140 mm.

Determine the percentage content of cadmium in metallic zinc.

19. The following data were obtained when taking a polarogram of a standard 0.0005*N* solution of zinc (the sensitivity of the polarograph was 20 μ A per 50 scale divisions):

| | | | | | |
|---|---|----|----|----|----|
| Volume of standard solution in 50 ml of back-ground, ml | 2 | 4 | 6 | 8 | 10 |
| Instrument reading | 6 | 14 | 22 | 30 | 37 |

When a 1.25-g sample of a metal containing zinc was dissolved and treated appropriately, 50 ml of the solution was obtained, for which the readings at the indicated sensitivity went beyond the scale. For this reason the sensitivity was decreased to 50 μ A per 50 scale divisions, and at this sensitivity the height of the zinc wave was 26.5 divisions.

Determine the percentage content of zinc in the metal.

20. When analysing a semiconducting alloy containing indium, cadmium, tin, and antimony a sample weighing 4.8 mg was dissolved in acid and after appropriate treatment the volume of the solution was made up to 10 ml with water. A 0.5-ml volume of the solution being analysed was diluted to 25 ml with a background solution and when running a polarogram the following wave heights for its components were obtained: antimony, 117 mm; tin, 7 mm; cadmium, 17 mm; and indium, 95 mm.

When running polarograms of standard solutions diluted with a background solution to 25 ml the following wave heights were obtained:

| | <i>V</i> , ml | <i>C</i> · 10 ⁴ , g/ml | <i>h</i> , mm |
|--------------|---------------|-----------------------------------|---------------|
| Sb | 0.5 | 1.75 | 91 |
| Sn | 0.3 | 1.011 | 32 |
| In | 0.5 | 1.77 | 93 |
| Cd | 0.3 | 1.011 | 33 |

Determine the percentage content of the components in the semiconducting alloy and the relative error of the determination.

21. Figure 65*a* is a plot of diffusion current versus pH for glyoxalic acid and Fig. 65*b* shows calibration graphs at different pH values and temperatures.

On the basis of these data determine the temperature coefficient for the diffusion current and the concentration

of glyoxalic acid in the solution (in moles per litre) at $\text{pH} = 10$ and a temperature of 25°C if the value of diffusion current is $45\ \mu\text{A}$.

22. When analysed by oscillographic polarography unitol gave the following anode peaks:

| | | | | | |
|-----------------------|----|----|----|----|----|
| C , mmole/litre . . | 4 | 8 | 12 | 16 | 20 |
| h , mm | 17 | 36 | 56 | 70 | 91 |

Unitol gives with zinc a stable, polarographically inactive complex with a ratio of $[\text{zinc}] : [\text{unitol}] = 1 : 2$.

Determine the concentration of zinc if the height of the unitol peak was 78 mm and after addition of 2.5 ml of the

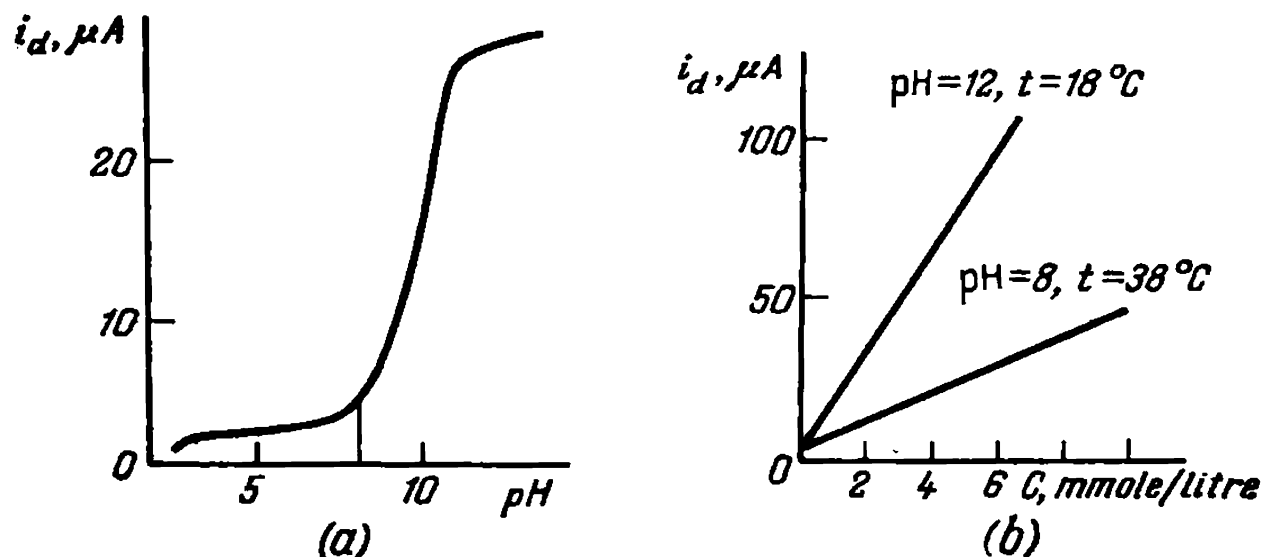


Figure 65

zinc solution being analysed to 10 ml of the unitol solution it dropped to 42.5 mm.

23. In the determination of antimony by the method of amalgam polarography the following anode peaks of dissolution were obtained depending on the concentration of antimony in the solution (the time of accumulation was 5 min):

| | | | | |
|-------------------------------|------|------|------|------|
| $C \cdot 10^6$, mole/litre | 0.25 | 1.10 | 2.7 | 5.0 |
| i , μA | 1.2 | 5.0 | 12.9 | 24.7 |

The following data were obtained when studying the dependence of the magnitude of the antimony peak on the time of accumulation for concentrations of 4×10^{-6} mole per litre:

| | | | | | |
|---------------------------|------|------|------|------|------|
| τ , min . . | 3 | 7 | 10 | 14 | 18 |
| i , μA . . . | 15.4 | 36.0 | 50.9 | 72.0 | 92.8 |

When a 0.55-g sample of a mineral was dissolved in 100 ml of acid, a peak was obtained at 45.6 μA for the time of accumulation 12 min.

Determine the percentage of antimony in the mineral.

SECTION B

24. To analyse a semiconducting alloy containing indium, cadmium, tin, and antimony, a sample of this alloy weighing 0.2270 g was dissolved in acid and after appropriate treatment the volume of the solution was made up to 250 ml with water. When running a polarogram of 1 ml of the solution prepared against the background of 6*N* hydrochloric acid the following wave heights were obtained: antimony, 172; tin, 32; indium, 147; and cadmium, 65 mm.

Standard solutions were made by dissolving samples of indium, cadmium, tin, and antimony weighing 0.0344, 0.0337, 0.0337, and 0.0350 g, respectively, and diluting each of them with water to 100 ml. To run polarograms 1 ml of an indium salt solution, 0.1 ml of a cadmium salt solution, 0.1 ml of a tin salt solution and 1 ml of an antimony salt solution were taken and diluted with a background solution to 25 ml. As a result, waves were obtained, with heights of 137, 50, 25 and 130 mm, respectively.

Determine the composition of the semiconducting alloy.

25. In a polarographic determination with a dropping-mercury electrode with $m = 2.14 \text{ mg/sec}$, $\tau = 4 \text{ sec}$ against the background of ammonium nitrate and a mixture of benzene and methanol the following values of limiting diffusion current were obtained for dicyclohexylperoxydicarbonate (CPC) at various concentrations:

| | | | | | |
|-----------------------------|-------|-------|-------|-------|-------|
| C , mmole/litre | 0.176 | 0.348 | 0.509 | 0.667 | 0.819 |
| i , μA | 1.44 | 2.78 | 4.11 | 5.45 | 6.56 |

Assuming that the diffusion coefficient for CPC is $D = 1.3 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$, determine the number of electrons participating in the reduction reaction and the concentration of CPC in the solution if with a capillary for which $m = 1.84 \text{ mg/sec}$ and $\tau = 4.3 \text{ sec}$ the diffusion current is equal to 3.58 μA .

26**. For diallylaminoethylmethacrylate (DAMA) the diffusion current constant against the background of dimethylformamide with water is $3.45 \mu\text{A}/\text{mmole}$ and after addition of an equal volume of phenol it becomes equal to $4.08 \mu\text{A}/\text{mmole}$. For diallylaminoethylacrylate (DAA) the corresponding values are 2.16 and $4.34 \mu\text{A}/\text{mmole}$. The diffusion current in a mixture of DAMA and DAA in dimethylformamide with water was found to be equal to $13.38 \mu\text{A}$ and after addition of an equal volume of phenol it decreased to $8.81 \mu\text{A}$.

Find the concentrations of DAMA and DAA in the solution (in mmoles per litre).

27**. In an oxalate solution in the presence of hydrogen peroxide and tantalum there appears a catalytic hydrogen current. The following data are obtained for the catalytic current versus the concentration of tantalum at 30°C and versus temperature:

| | | | | |
|--|------|------|------|------|
| $C_{\text{Ta}} \times 10^3$, mole/litre . . | 0.04 | 0.08 | 0.12 | 0.16 |
| i , μA | 0.31 | 0.59 | 0.95 | 1.22 |
| Temperature, $^\circ\text{C}$. . | 25 | 41 | 50 | 60 |
| i , μA | 0.68 | 1.70 | 2.98 | 5.05 |

In the solution being analysed at 45°C the catalytic current was found to equal $2.48 \mu\text{A}$.

Determine the concentration of tantalum in the solution (in mmoles per litre).

28. In the polarographic determination of tungsten with a mercury drop having a mass of 8.56 mg, the drop time being 4 sec, the following data were obtained at various concentrations of tungsten:

| | | | | | |
|---------------------------------|------|-----|------|------|------|
| C , mmole/litre . . | 1.19 | 4.8 | 8.3 | 11.9 | 15.5 |
| i_d , μA | 2.25 | 8.5 | 17.0 | 25 | 33 |

Determine the average value of the diffusion coefficient of tungsten and the error of the determination if the electrode process corresponds to the transition $\text{W}^{6+} \rightarrow \text{W}^{5+}$.

29**. The following relation between the height of the polarographic wave and the height of the mercury column was observed for the ion Mn^{2+} against the background of potassium chloride and sulphosalicylic acid:

| | | | | |
|----------------------|------|------|------|------|
| h , mm . . | 21.5 | 26.0 | 30.0 | 34.5 |
| h_{Hg} , mm | 160 | 250 | 360 | 490 |

The height of the manganese wave varies depending on its concentration at $H_{\text{Hg}} = 360$ mm in the following way:

| | | | | | |
|--------------------------------------|-----|------|----|------|----|
| $C \cdot 10^3$, moles per litre . . | 1 | 2 | 3 | 4 | 5 |
| h , mm | 8.5 | 16.5 | 24 | 31.5 | 40 |

Check the diffuse nature of the reduction process and find the concentration of manganese in the solution (in mg/ml) if for the height of the mercury column 250 mm the wave height is 20 mm.

30**. The following values of half-wave potentials were obtained in investigating the process of formation of complexes of cadmium and iodide as a function of the concentration of ligand:

| | | | | | | |
|---------------------|--------|--------|--------|--------|--------|--------|
| C , mole/litre | 0 | 0.1 | 0.3 | 0.6 | 0.9 | 1.2 |
| $E_{1/2}$, V . . . | -0.594 | -0.639 | -0.689 | -0.719 | -0.737 | -0.755 |

| | | | |
|-------------------------|--------|--------|--------|
| C , mole/litre . . . | 1.5 | 2.7 | 3.0 |
| $E_{1/2}$, V | -0.785 | -0.794 | -0.804 |

Determine the coordination number of Cd^{2+} and the complex-formation constant.

31**. In a polarographic investigation of pyridinic complexes of copper, for the second reduction wave the following values were obtained for $E_{1/2}$ versus the concentration of pyridine:

| | | | | |
|---------------------------------------|--------|--------|--------|--------|
| $C_{\text{pyr}} \cdot 10^2$, M . . | 1.58 | 3.81 | 8.25 | 13.3 |
| $E_{1/2}$, V . . . | -0.263 | -0.309 | -0.356 | -0.380 |

| | | | |
|--|--------|--------|--------|
| $C_{\text{pyr}} \cdot 10^{-1}$, M . . | 3.55 | 6.73 | 8.97 |
| $E_{1/2}$, V | -0.445 | -0.490 | -0.532 |

| | | | | |
|----------------------------|--------|--------|--------|--------|
| C_{pyr} , M . . | 1.35 | 1.79 | 2.02 | 2.24 |
| $E_{1/2}$, V . . | -0.561 | -0.592 | -0.600 | -0.608 |

Draw a conclusion as to the nature of the complex-formation process and find the coordination numbers of copper and the stability constants of the complexes.

4. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. In which cases is it expedient to use amalgam polarography with accumulation?

(a) When high concentrations of ions are to be determined.

(b) When one has to determine small concentrations of metals that are reducible to metals with the formation of an amalgam.

(c) If one has to determine ions that are reducible at very negative potentials.

(d) If one has to determine small concentrations of anions that are reducible to cations.

(e) If one has to determine small concentrations of ions that are reducible from the highest to the lowest valency.

2. A substance gives a polarographic wave at a half-wave potential of 0.5 V and the titrant gives a wave with a half-

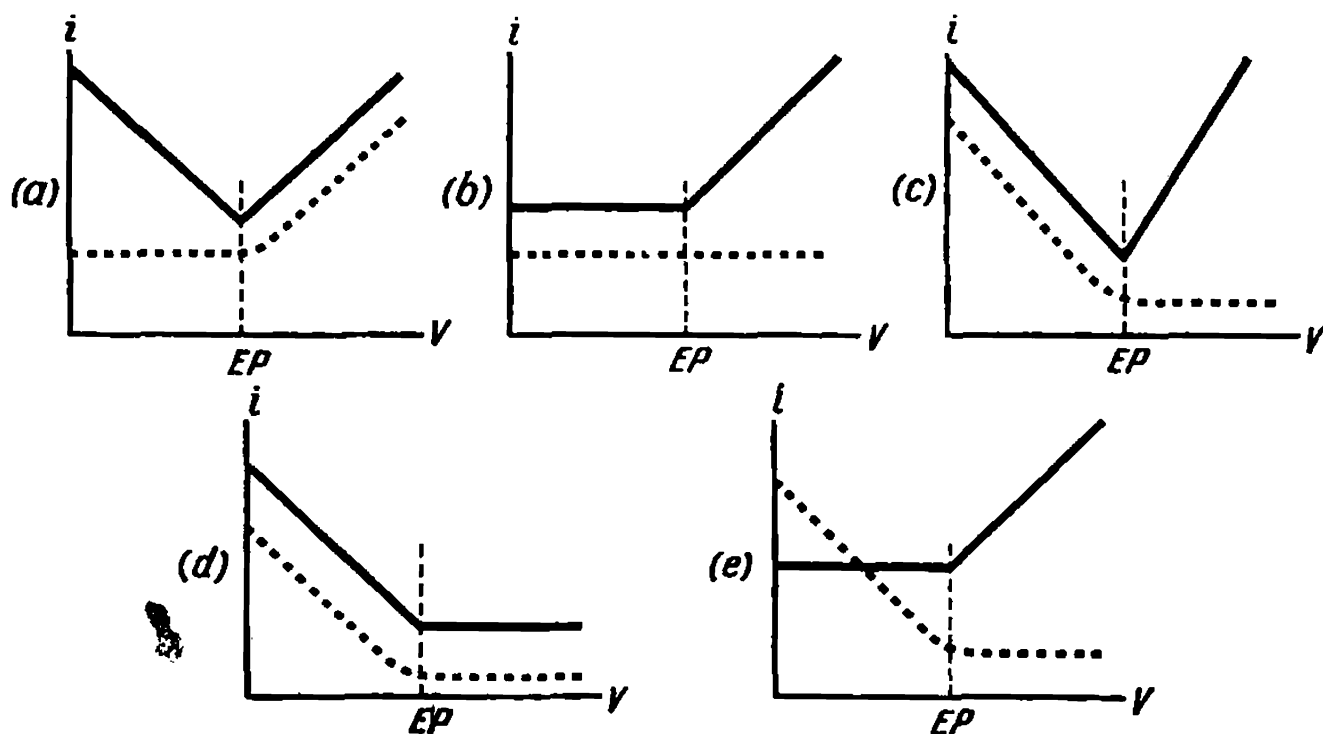


Figure 66

wave potential of 0.9 V. Among the graphs of amperometric titration given in Fig. 66 at 0.75 V (.....) and at 1.1 V (—) find the correct one.

3. In a 25-ml cell the magnitude of the diffusion current of lead is 20 μ A. After the addition of 1 ml of a standard solution in which the concentration of lead is 5 μ g/ml the diffusion current increases to 25 μ A. Which of the following formulas can be used to determine the unknown concentration?

$$(a) \quad C_x = \frac{5 \times 1 \times 20}{25 - 20} = 20 \mu\text{g/ml.}$$

$$(b) \quad C_x = \frac{5 \times 2 \times 20}{25} = 8 \mu\text{g/ml.}$$

$$(c) \quad C_x = \frac{5}{\frac{20}{25} \times \frac{10}{1} - \frac{10}{1}} = 0.63 \mu\text{g/ml.}$$

$$(d) \quad C_x = \frac{5}{\frac{25}{20} \times \frac{10+1}{1} - \frac{10}{1}} = 3.7 \mu\text{g/ml.}$$

(e) The data given are insufficient for determination of the unknown concentration.

4. Indicate the answers as to what methods could be used to eliminate maxima of various kinds.

(a) Maxima of the first and second kinds are eliminated by introducing surface-active substances.

(b) A maximum of the first kind can be eliminated by raising the temperature.

(c) A maximum of the third kind can be eliminated by decreasing the rate of imposition of the potential.

(d) A maximum of the first kind can be eliminated by decreasing the speed of tracing a polarogram.

(e) Maxima of the second and third kinds cannot be eliminated by any method.

(f) Maxima of the third and fourth kinds arise only on solid electrodes and cannot be suppressed by means of surface-active substances.

(g) All the maxima can be eliminated by introducing surface-active substances.

(h) Maxima of the third and fourth kinds that arise on mercury electrodes cannot be eliminated by surface-active substances.

5. The solution being titrated contains two cations, A^+ and B^+ , whose polarograms are shown in Fig. 67. The same figure shows the polarogram of the titrant X^- . Find the correct answers as to the shapes of the curves of amperometric titration of these cations under the conditions indicated.

(a) Potential 0.8 V; $SP_{AX} \gg SP_{BX}$ (Fig. 68).

(b) Potential 0.8 V; A^+ does not react with X^- (Fig. 69).

(c) Potential 1.1 V; $SP_{AX} \ll SP_{BX}$ (Fig. 70).

(d) Potential 0.8 V; $SP_{AX} \ll SP_{BX}$ (Fig. 71).

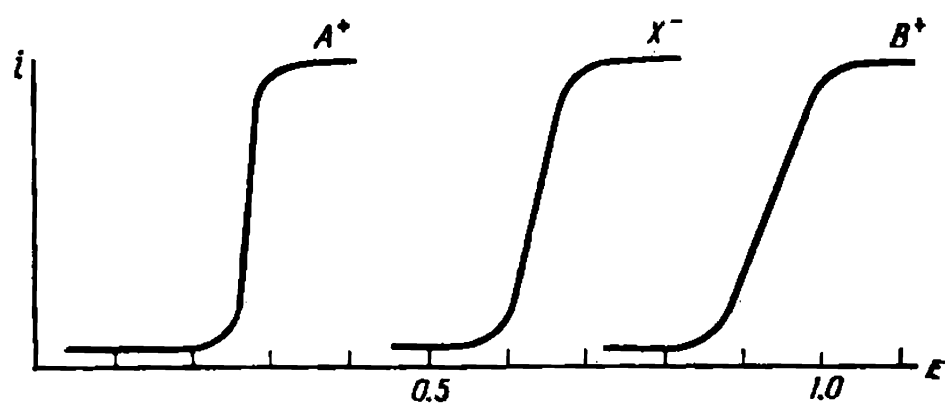


Figure 67

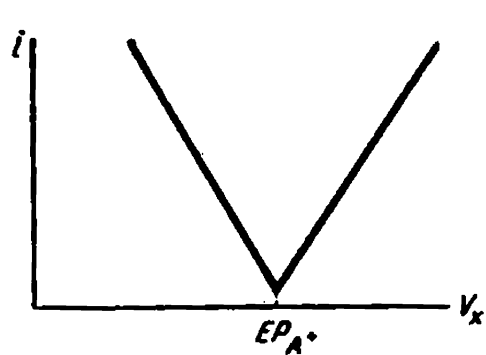


Figure 68

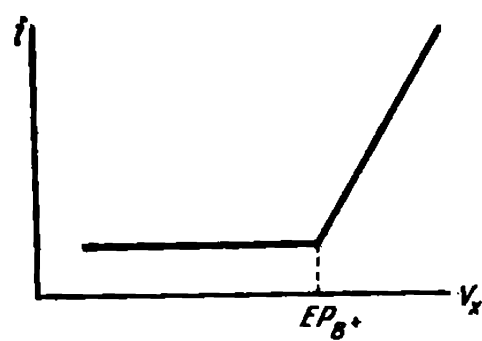


Figure 69

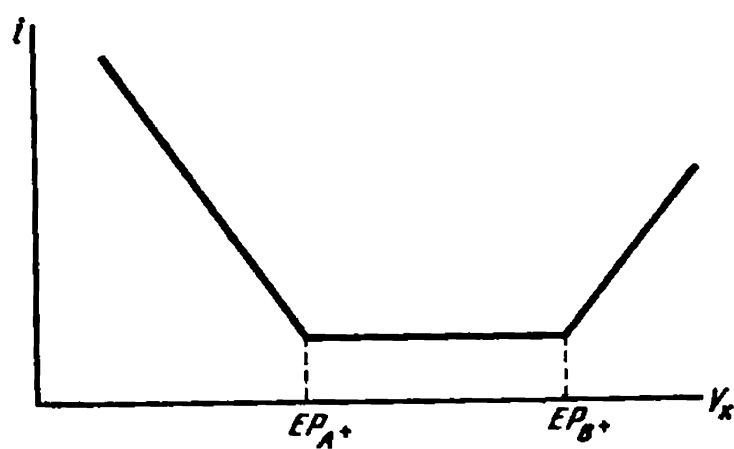


Figure 70

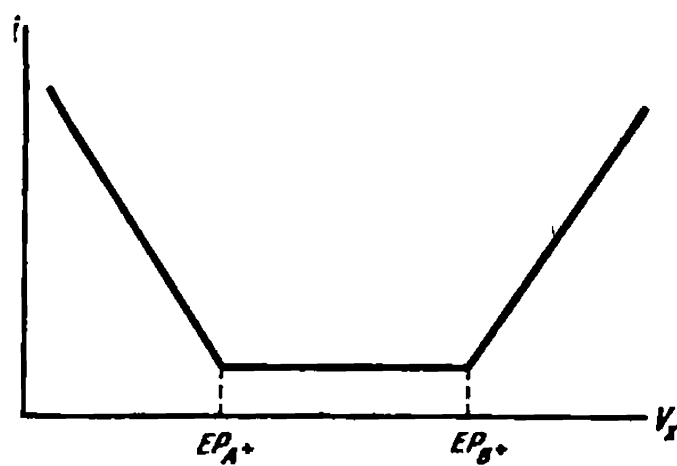


Figure 71

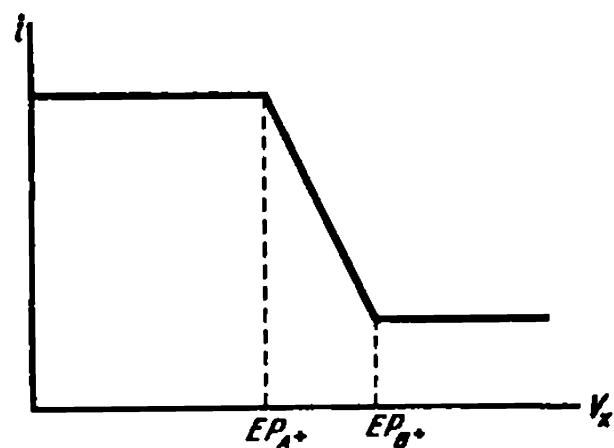


Figure 72

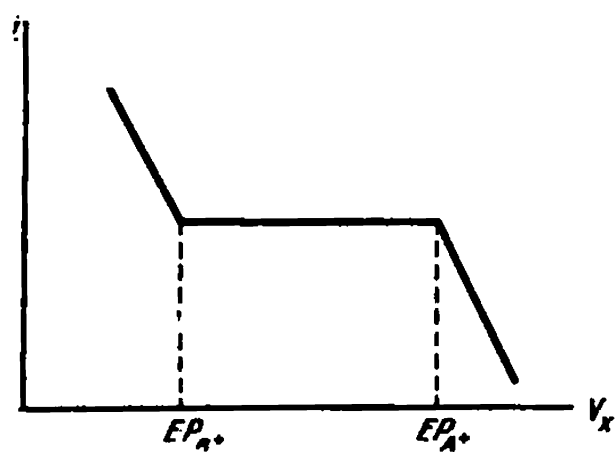


Figure 73

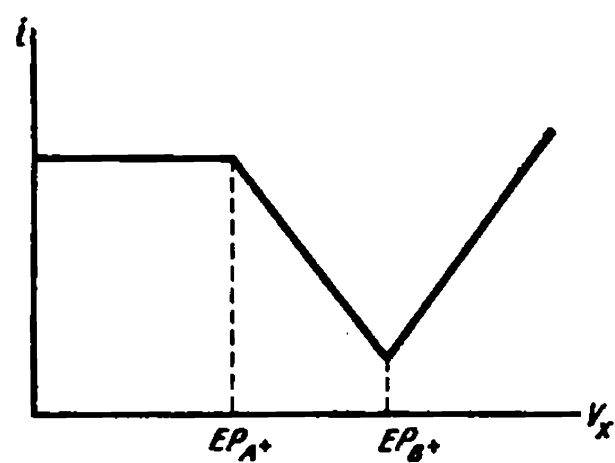


Figure 74

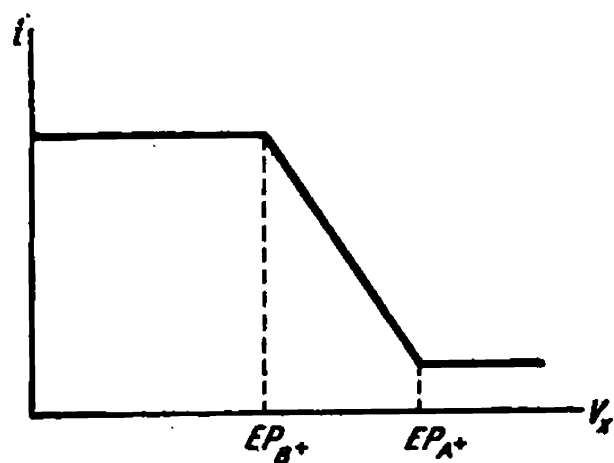


Figure 75

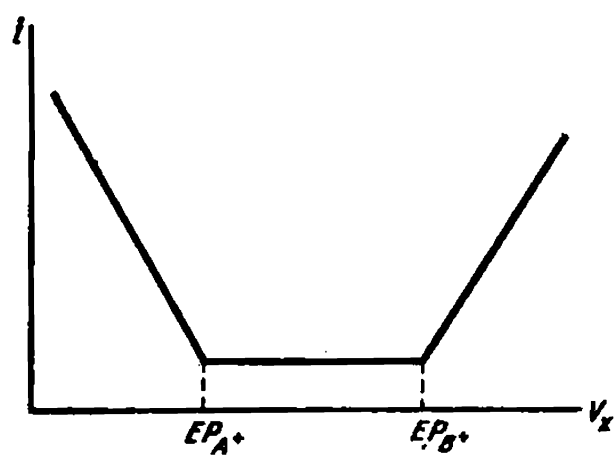


Figure 76

- (e) Potential 0.4 V; $SP_{AX} \gg SP_{BX}$ (Fig. 72).
- (f) Potential 1.2 V; $SP_{AX} \gg SP_{BX}$ (Fig. 73).
- (g) Potential 0.8 V; $SP_{AX} \ll SP_{BX}$ (Fig. 74).
- (h) Potential 0.4 V; $SP_{AX} \gg SP_{BX}$ (Fig. 75).
- (i) Potential 1.1 V; B^+ does not react with X^- (Fig. 76).

6. Find under B the definition, and under C the ways for eliminating or decreasing the polarographic currents indicated under A.

A

- (a) Condenser (charging) current.
- (b) Migration current.
- (c) The limiting current.
- (d) Kinetic current.
- (e) Diffusion current.

B

(1) The current at the mercury electrode caused by the movement of the surface of a mercury drop.

(2) The current caused by the diffusion of the ion being determined to the electrode.

(3) The current arising from the movement of the ion to be determined under the influence of the imposed electric field.

(4) The current resulting from the diffusion of the background electrolyte to the electrode.

(5) The current at the solid electrode associated with the conditions under which the polarogram is traced.

(6) The current caused by the movement of the liquid around the solid electrode.

(7) The current for charging the surface of the mercury drop.

(8) The current controlled by the chemical reactions taking place in the near-electrode layer.

(9) The current for charging the surface of the platinum electrode.

C

(1) This current can neither be eliminated nor reduced; it is used in polarographic analysis.

(2) This current is reduced by addition of a background electrolyte.

(3) This current is eliminated by changing the composition of the background. In some cases it is used in analysis.

(4) This current can be eliminated by raising the temperature.

(5) At the mercury electrode this current is eliminated by addition of surface-active substances.

(6) This current is eliminated by tracing a polarogram at the moment when the size of the drop is maximal.

(7) This current is eliminated by increasing the rate of drop formation.

(8) This current is eliminated by means of special arrangements.

(9) This current can neither be eliminated nor reduced.

7. Using the handbook, find under B the half-wave potentials $E_{1/2}$ and under C the diffusion current constants $K = \log/Cm^{2/3} \tau^{1/6}$ for the electrode processes listed under A.

A

| Process | Background |
|---|--|
| (a) $\text{Cd}^{2+} \rightarrow \text{Cd}$ | 1M HCl + 0.01 per cent gelatin |
| (b) $\text{NO}_3^- \rightarrow 1/2\text{N}_2$ | 0.1M KCl + 0.01M HCl + 2×10^{-4} M UO_2Cl_2 |
| (c) $\text{Sn}^{3+} \rightarrow \text{Sn}^{2+}$ | 0.1M $(\text{CH}_3)_4\text{NI}$ + 0.001M H_2SO_4 + 0.01 per cent gelatin |
| (d) $\text{V}^{5+} \rightarrow \text{V}^{4+}$ | 1M NH_3 + 1N NH_4Cl + 0.005 per cent gelatin |
| (e) Benzil | 50 per cent $\text{C}_2\text{H}_5\text{OH}$; pH = 1.3 |
| (f) Stilbene | 0.175M $(\text{C}_4\text{H}_9)_4\text{NI}$ + 75 per cent dioxane |
| (g) $2\text{S}_2\text{O}_3^{2-} + \text{Hg} \rightarrow \text{Hg}(\text{S}_2\text{O}_3)_2^{2-}$ | 0.1N KNO_3 |

B

C

| | |
|-------------|--------------|
| (1) -1.80. | (1) 13.95. |
| (2) -0.27. | (2) 4.72. |
| (3) -0.98. | (3) 3.51. |
| (4) -0.599. | (4) 3.85. |
| (5) -2.26. | (5) No data. |
| (6) -0.97. | |
| (7) -0.15. | |

8. Find under B the characteristic and under C the calculation formula for the methods of quantitative polarographic determination listed under A.

A

- (a) The internal standard method.
- (b) Amperometric titration.
- (c) The calculation method.
- (d) The calibration graph method.
- (e) The polarographic method with accumulation.
- (f) The standard addition method.
- (g) Amperometric titration with the use of an indicator.

B

(1) In this method, the limiting current is determined for a number of concentrations and then the unknown concentration is found from the graph.

(2) Limiting currents are determined for two standard solutions whose concentrations are respectively higher and lower than the unknown concentration and the calculation is made from the limiting current of the unknown solution.

(3) The slope of the I_{lim} vs. C line is calculated and the equation obtained is used for calculation.

(4) The limiting current is determined for the unknown concentration, a certain volume of the standard solution is added, and the new limiting current is determined. The unknown concentration is calculated from these two values.

(5) The ion to be determined is titrated with a reagent and then the equivalence point and the unknown concentration are determined from the inflection point on the h vs. V graph.

(6) The limiting currents are determined for two standard solutions, the data obtained are plotted and the graph obtained is used to find the unknown concentration.

(7) At a potential higher than the half-wave potential the metal being determined is deposited on a mercury drop and its concentration is determined from the magnitude of the anodic dissolution peak.

(8) The limiting current is determined for one portion of the solution under study, and to another is added a certain volume of the standard solution and the limiting current is determined again. The data obtained are used to calculate the unknown concentration.

(9) The unknown concentration is calculated from the

table data on the diffusion coefficient and the conditions under which the drop is formed.

(10) A polarographically active indicator is added to the solution under study and the equivalence point is determined from the plot of the variation of its wave height against the volume of added reagent and the unknown concentration is calculated.

C

$$(1) \quad C_x = \left(\frac{C_1}{i_1} + \frac{C_2}{i_2} \right) \frac{i_x}{2}.$$

$$(2) \quad C_x = K i_x.$$

$$(3) \quad C_x = \frac{C_2 (i_x - i_1) - C_1 (i_2 - i_x)}{i_2 - i_1}.$$

$$(4) \quad C_x = \frac{C_1 i_x}{i_1} = \frac{C_2 i_x}{i_2}.$$

$$(5) \quad C_x = \frac{i_x}{605 n D^{1/2} m^{2/3} \tau^{1/6}}.$$

$$(6) \quad C_x = TV.$$

$$(7) \quad C_x = \frac{(C_1 + C_2) i_x}{i_1 + i_2}.$$

$$(8) \quad C_x = \frac{C_{st}}{\frac{i'}{i_x} \frac{V_x + V_{st}}{V_{st}} - \frac{V_x}{V_{st}}}.$$

$$(9) \quad C_x = \frac{C_{st} i_x}{i' - i_x}.$$

9. Find under A the correct answers as to what purposes the following equation of the polarographic wave can be used for:

$$E = E_{1/2} - \frac{0.058}{z} \log \frac{i}{i_d - i}$$

Indicate under B the conditions in which this equation cannot be used.

A

(a) For determination of the number of electrons participating in the electrochemical process.

(b) For checking calibration graphs,

(c) For determination of the concentration by the calculation method.

(d) For determination of the half-wave potential of any process.

(e) For determination of the number of electrons participating in any electrochemical reaction.

(f) It can be used in combination with the coulometric method for determination of the degree of reversibility of the process.

(g) For determination of the degree of reversibility of the process.

(h) The equation itself is not used for calculations, but it enables one to derive other important polarographic equations.

B

(1) This equation is inapplicable to small concentrations of depolarizers.

(2) This equation is inapplicable to the stationary mercury drop.

(3) This equation can be used only at temperatures not higher than 30 °C.

(4) The possibility of using this equation depends on the height of the mercury column; it must not exceed 40 cm.

(5) This equation is inapplicable to curves with maxima.

(6) This equation is inapplicable to fast-dropping capillaries.

(7) This equation is inapplicable to solid platinum and graphite electrodes.

(8) The use of this equation is limited by no factors.

10. Can the internal standard method be used in those cases when the line representing the dependence of the limiting current on the concentration does not pass through the coordinate origin? Find under A the correct answer to this question, and under B the calculation formula for this case.

A

(a) In this case use may be made of the internal standard method, just as in the case when the straight line passes through the origin.

(b) In this case not one but two standards with desirable concentrations $C_1 < C_x < C_2$ must be traced polarographically.

(c) In this case it is necessary to trace polarographically several standard solutions with concentrations higher than the one being determined:

$$C_x < C_1 < C_2 < C_3 < C_4$$

(d) In this case it is necessary that the standard solution be more concentrated than the one under study: $C_x \ll C_{st}$.

(e) In this case the internal standard method cannot be used.

B

$$(1) \quad C_x = C_{st} \frac{i_x}{i_{st}}.$$

$$(2) \quad C_x = C_{st} \frac{4i_x}{i_1 + i_2 + i_3 + i_4}.$$

$$(3) \quad C_x = \frac{C_2(i_x - i_1) - C_1(i_2 - i_x)}{i_2 - i_1}.$$

$$(4) \quad C_x = \frac{1}{2} \left(\frac{C_1}{i_1} + \frac{C_2}{i_2} \right) i_x.$$

(5) The calculation formula cannot be derived.

5. ASSIGNMENTS IN ELECTROCHEMICAL METHODS OF ANALYSIS FOR TEACHING MACHINES

FIRST ASSIGNMENT. Work up the section on the theory of the potentiometric method in your textbook.

Main question. A system of galvanic cells is built up (see Fig. 77a). The indicator used is a differential galvanometer with two coils which are so arranged that the galvanometer registers the difference of potentials applied to it.

What will the galvanometer show during the titration with equal volumes of titrant if the initial concentrations of the solutions being titrated in both vessels are equal? What reactions will take place in these vessels? Will it be possible to detect the attainment of the equivalence point in each vessel by galvanometer readings?

Indicate the correct answer.

(a) The galvanometer needle will not deflect and the determination of the equivalence points is impossible.

(b) The galvanometer needle will pass through the zero point in the course of titration and only a total titration curve can be plotted on the basis of the readings.

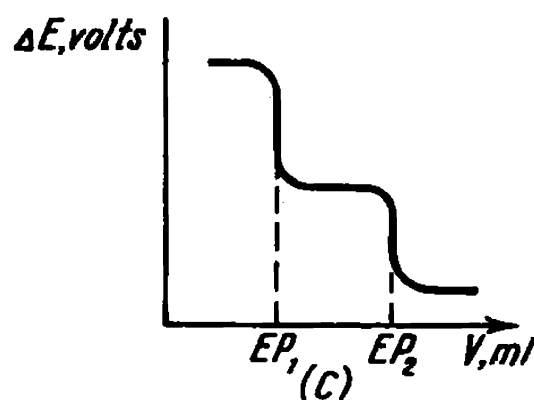
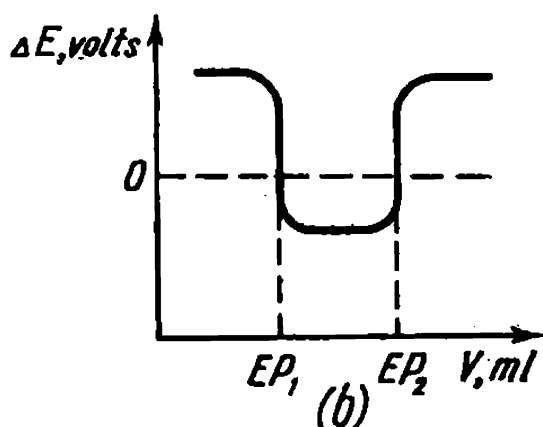
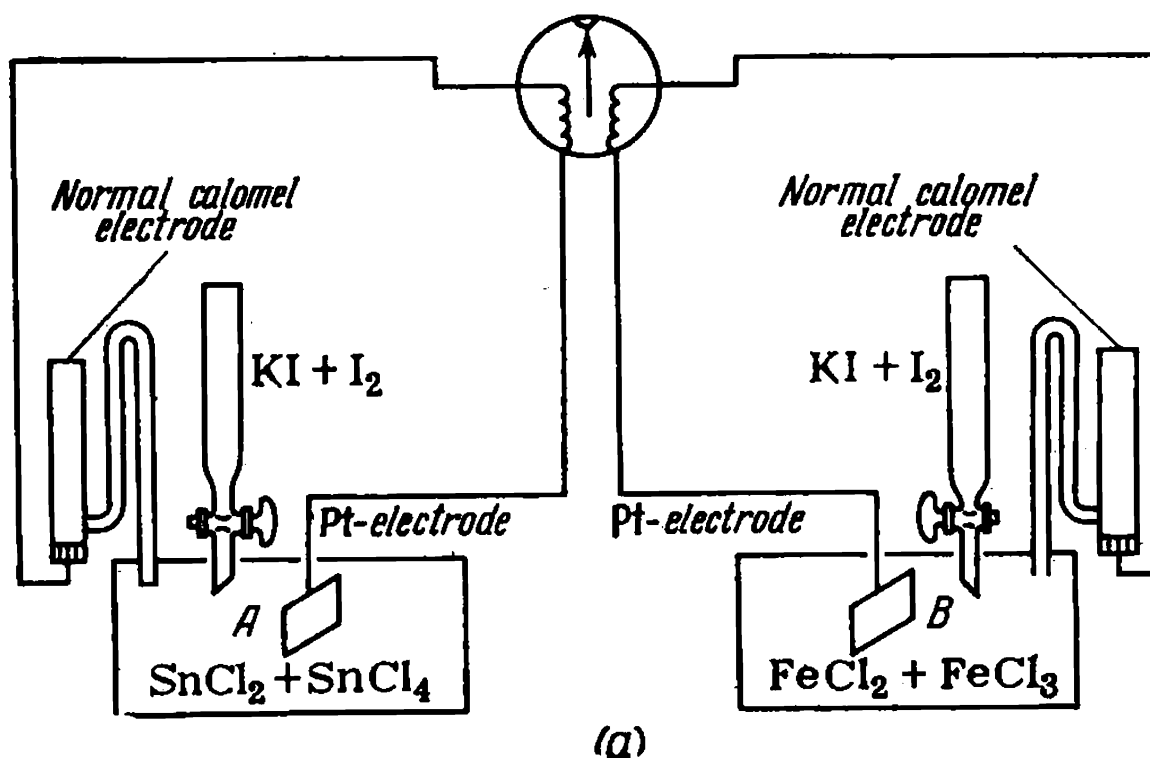


Figure 77

(c) The galvanometer readings will correspond to the equivalence points twice during the titration, the needle will pass through the zero, and the titration graph will look like the one shown in Fig. 77b.

(d) The galvanometer readings will change, and the needle will deflect to one side. At different concentrations of the solutions being titrated the titration graph will look like the one shown in Fig. 77c.

At equal concentrations the two curves will merge into one.

If your answer is correct, pass over to the next assignment, and in case you fail to give the correct answer, try to answer the first additional question.

First additional question. Determine the values of the potentials of platinum electrodes in vessels *A* and *B* and construct

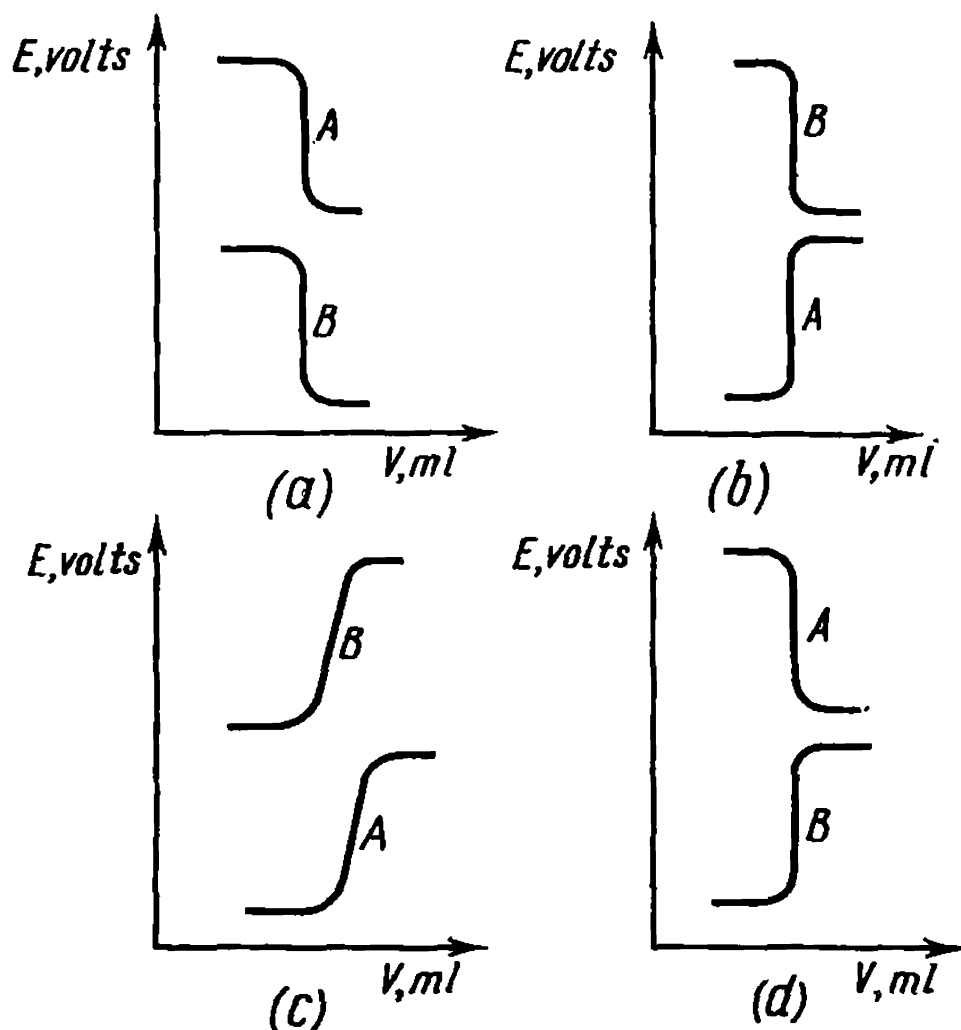


Figure 78

titration curves for vessels *A* and *B* separately. Compare your answer with the titration curves given in Fig. 78.

If your answer is correct, pass over to the second additional question. And in case your answer is wrong you are to recapitulate the theory of potentiometric titration.

Second additional question. By referring to the circuit shown in Fig. 77a indicate how the currents will flow through the galvanometer and how they will change in the two vessels in the course of titration.

(a) The currents flow through the galvanometer in opposite directions. A difference of potentials will be noted between the systems *A* and *B* during the titration.

(b) The currents flow through the galvanometer in one direction, but since the titration curves are of different shape the galvanometer will show the difference in the potentials of the systems *A* and *B*.

(c) The currents flow through the galvanometer in a single direction and the galvanometer registers the sum of the potentials of the systems *A* and *B*; if the titration curves are shifted one relative to the other, the galvanometer will indicate two titration jumps.

(d) The currents flow through the galvanometer in one direction and the galvanometer registers the sum of the potentials of the systems *A* and *B*. In all cases the galvanometer will register the total titration jump.

If your answer is correct, pass over to the next assignment. If you fail to answer the question correctly, you are to recapitulate the theory of the potentiometric method.

SECOND ASSIGNMENT. Work up the section "Quantitative polarographic analysis" in your textbook.

Main question. Can one use the internal standard method and the method of standard addition for a quantitative polarographic determination if the calibration curve does not pass through the origin of an *h* vs. *C* plot? Derive the necessary formulas for calculation and use them to solve the following:

Standard addition method

$$h_x = 15 \text{ mm}$$

$$\text{1st addition } \Delta C_1 = 2 \text{ } \mu\text{g/ml}$$

$$h_1 = 22.5 \text{ mm}$$

$$\text{2nd addition } \Delta C_2 = 4 \text{ } \mu\text{g/ml}$$

$$h_2 = 30 \text{ mm}$$

Internal standard method

$$h_x = 5 \text{ mm}$$

$$C_1 = 6 \text{ } \mu\text{g/ml}; \quad h_1 = 7 \text{ mm}$$

$$C_2 = 9 \text{ } \mu\text{g/ml}; \quad h_2 = 9 \text{ mm}$$

(a) Neither method can be used in this case.

(b) The internal standard method may be used. $C_x = 3 \text{ } \mu\text{g/ml}$. The standard addition method is inapplicable.

(c) Both methods are applicable. By the standard addition method $C_x = 4 \text{ } \mu\text{g/ml}$, and by the internal standard method $C_x = 2 \text{ } \mu\text{g/ml}$.

(d) The standard addition method may be used, $C_x = 4 \mu\text{g/ml}$, and the internal standard method is inapplicable.

If the answer is correct, pass over to the next assignment. And if you fail to give the correct answer, try to answer the additional question.

Additional question. Taking into account that the height of a polarographic wave is connected with the concentration by the linear relation $h = a + bC$, deduce formulas for calculating C_x for both methods and compare them with those given below.

(a) An identity is obtained for the standard addition method.

For the internal standard method the following equation is obtained:

$$C_x = \frac{C_2 (h_x - h_1) - C_1 (h_2 - h_x)}{h_2 - h_1}$$

(b) The equation obtained for the standard addition method is

$$C_x = \frac{C_{st}}{\frac{h_1 + h_2}{2h_x} \cdot \frac{V_{st} + V_x}{V_{st}} - \frac{V_x}{V_{st}}}$$

For the internal standard method we have an identity.

(c) For both methods the second additions are not needed and one can use ordinary formulas.

The standard addition method:

$$C_x = \frac{h_x}{h_1 - h_x} \cdot \Delta C_1 = \frac{h_x}{h_2 - h_x} \cdot \Delta C_2$$

The internal standard method:

$$C_x = \frac{h_x}{h_1} \cdot C_1 = \frac{h_x}{h_2} \cdot C_2$$

(d) No equation for calculation can be derived for either method.

If your answer is correct, pass over to the main question; in case you fail to give the correct answer, work up again the section "Polarography" and recapitulate the section in mathematics "Derivation of the equations of straight lines".

THIRD ASSIGNMENT. Work up the theory of amperometric titration.

Main question. The solution being titrated contains three cations, of which A^+ and B^+ give polarographic waves shown in Fig. 79a, and the cation C^+ is polarographically inactive. The titration is carried out with a solution of HX , with the

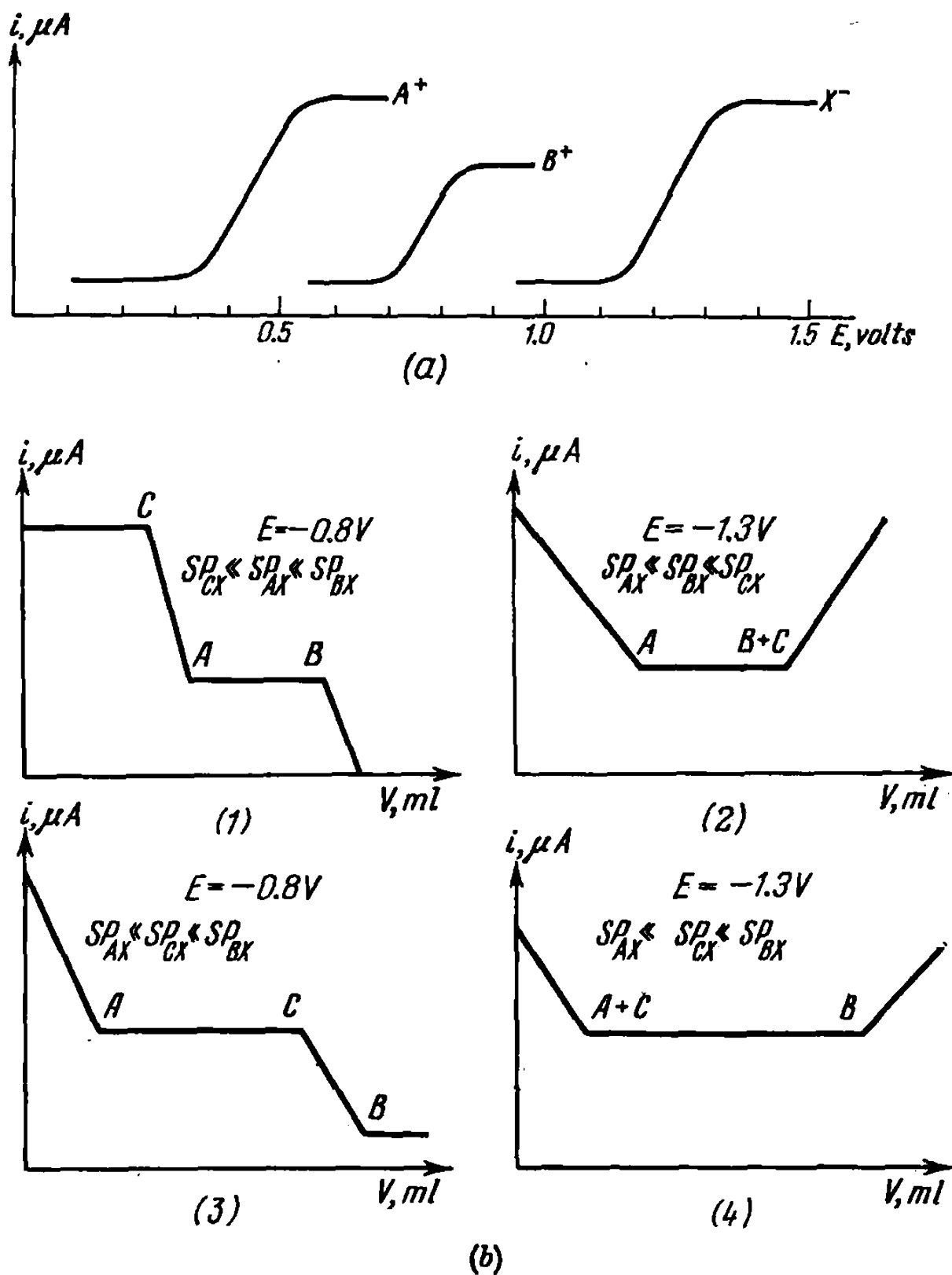


Figure 79

anion of which all the three cations form precipitates. The anion X^- has a polarographic wave shown in Fig. 79a.

Find out, according to the ratios of the solubility products of the precipitates formed (see Fig. 79b), which of the titration curves reflects correctly the process of titration at the indicated potential.

If your answer is correct, pass over to the next assignment and if it is wrong, give an answer to the additional question.

Additional question. Consider the titration curves, in Fig. 80, of each of the substances indicated at different

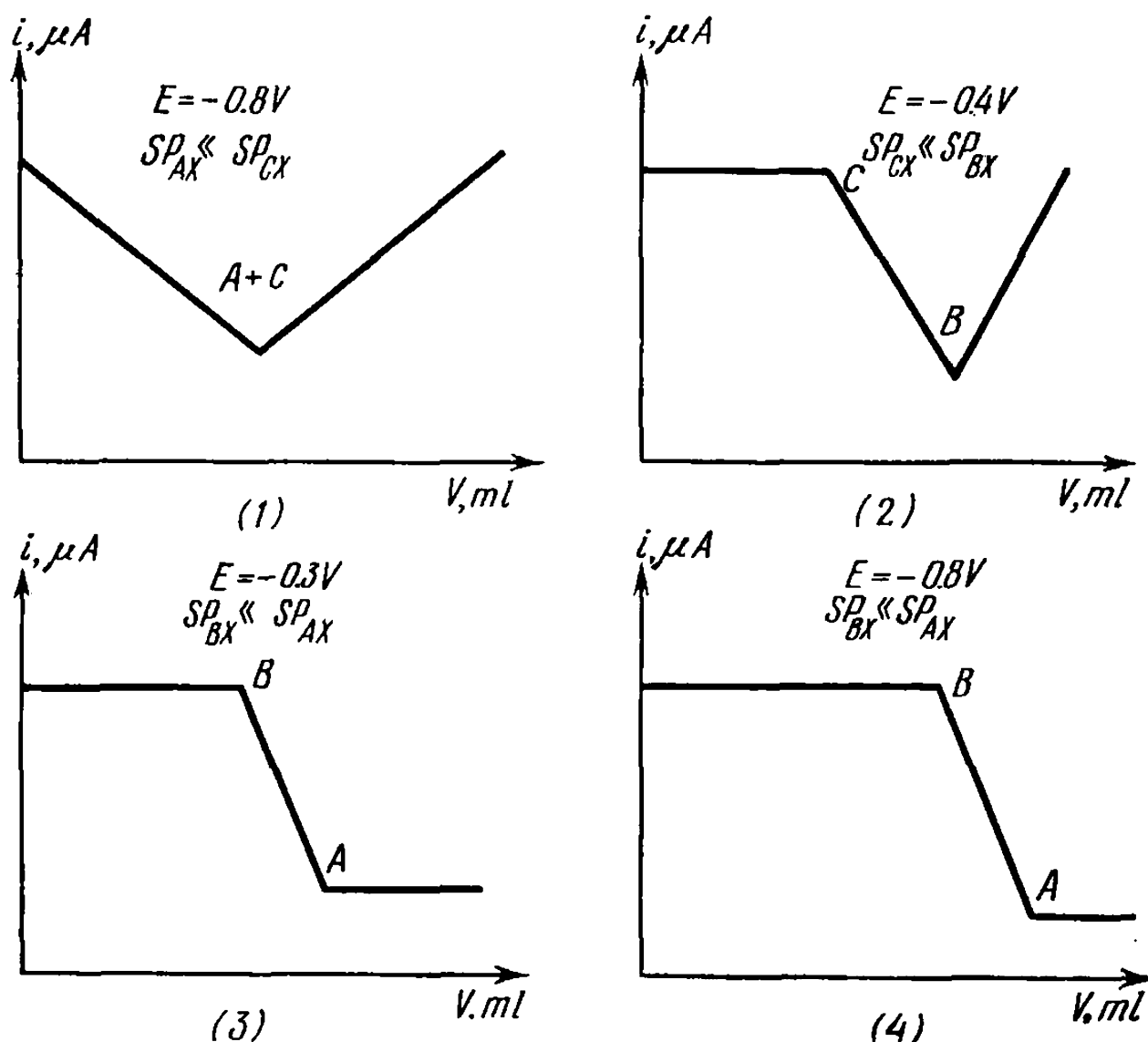


Figure 80

potentials and find out which of the graphs of titration of two components is correct.

If your answer is correct, turn back to the main question and if it is incorrect, work up again the theory of amperometric titration.

Other Methods of Analysis

This chapter includes problems covering thermogravimetric, mass-spectroscopic and radiochemical methods of analysis. Problems of only two types are given (A and B), multivariant problems being omitted.

1. EXAMPLES OF PROBLEM-SOLVING

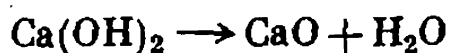
Example 1. In analysing a 250-mg sample of technical calcium hydroxide containing calcium carbonate and SiO_2 by the thermogravimetric method the following losses in mass were detected at various temperature ranges: loss of hygroscopic water (18 mg) at 100 to 150 °C; dehydration of calcium hydroxide (38 mg) at 510 to 560 °C; dissociation of calcium carbonate (22 mg) at 900 to 950 °C.

Determine the composition of technical calcium hydroxide.

Solution: We determine the content of hygroscopic water:

$$\frac{18 \times 100}{250} = 7.2\%$$

From the loss of mass at the interval 510-560 °C we find the content of calcium hydroxide:

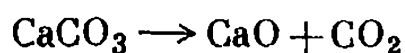


$$\frac{38 \times 74}{18} = 156 \text{ mg}$$

or

$$\frac{156 \times 100}{250} = 62.4\%$$

From the loss in mass at the interval 900-950 °C we find the content of calcium carbonate:



$$\frac{22 \times 100}{44} = \text{mg}$$

or

$$\frac{50 \times 100}{250} = 20\%$$

Hence the content of SiO_2 is equal to

$$100 - 7.2 - 62.4 - 20 = 10.4\%$$

Example 2. In the neutron-activation determination of selenium in copper a standard sample with a selenium concentration of 0.75 $\mu\text{g/g}$ and the unknown sample were subjected to bombardment with neutrons for 10 hours. The data on the intensity of gamma-radiation in the region of 0.05-0.2 MeV (megaelectron-volt) are indicated below:

| | | | | | | | | | | |
|--------------------------|------|------|------|------|------|------|------|------|------|------|
| E , MeV | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 | 0.22 |
| Number of counts: | | | | | | | | | | |
| standard | 400 | 400 | 500 | 900 | 1600 | 1400 | 800 | 600 | 400 | 400 |
| unknown sample | 600 | 600 | 900 | 1700 | 2800 | 3400 | 1200 | 700 | 600 | 600 |

Determine the content of selenium in the sample if the intensity of the gamma-radiation of the background in investigating the standard sample is 400 and that of the unknown sample, 600 counts per minute.

Solution: Taking into account the background counting rate for the standard (400 counts per minute) and for the unknown sample (600 counts per minute), we calculate the areas of the peak in terms of arbitrary units, say, at $E = 0.10$ MeV for the standard:

$$S = (900 - 400) 0.02 = 10$$

As a result, we obtain:

| | | | | | | | | | | |
|---------------------------|------|------|------|------|------|------|------|------|------|------|
| E | 0.04 | 0.06 | 0.08 | 0.10 | 0.12 | 0.14 | 0.16 | 0.18 | 0.20 | 0.22 |
| S_{st} | — | — | 2 | 10 | 24 | 20 | 8 | 4 | — | — |
| S_0 | — | — | 6 | 22 | 44 | 56 | 12 | 2 | — | — |

The total area is

$$\Sigma S_{st} = 68$$

$$\Sigma S_0 = 142$$

The content of selenium is equal to

$$\frac{0.75 \times 142}{68} = 1.57 \text{ } \mu\text{g/g}$$

Example 3. To a solution containing silver ions was added 50 μg of radioactive silver having an activity of 15,000 counts per minute. After the precipitation of the whole of silver as the chloride the activity of the precipitate was found to be equal to 120 counts per minute.

Determine the content of silver ions in the solution.

Solution: We make use of the formula for the isotope-dilution analysis. Since the activity changed considerably, we may use the approximate formula

$$x = g_{st} \frac{A_0}{A_i}$$

where g_{st} is the mass of the radioactive isotope added; A_0 is the initial activity of the isotope; and A_i is the activity of the precipitate formed.

Substituting the data given, we obtain:

$$x = 50 \times \frac{15,000}{120} = 6250 \text{ } \mu\text{g}$$

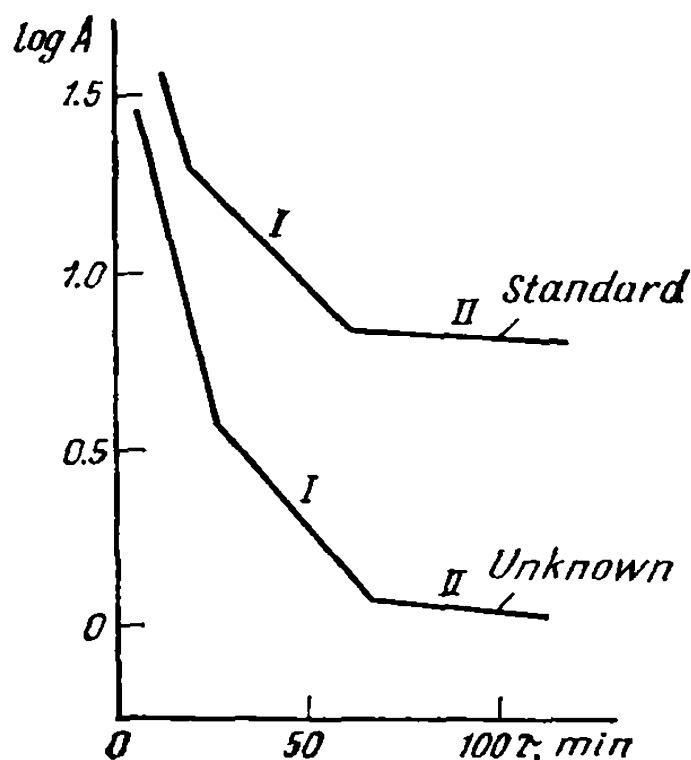


Figure 81

Example 4. In the determination of manganese and gadolinium in semiconducting alloys by radioactivation

analysis use was made of the isotope ^{55}Mn with a decay period (half-life) of 2.6 hours and ^{147}Gd with a half-life of 14 hours. The activities of the remainder constituents of the alloy may be ignored. The graph showing the change of the activity with time is shown in Fig. 81. The portion I corresponds to the decay of ^{55}Mn and the portion II to that

of ^{71}Gd . The curve of the variation of activity for the reference standard sample containing 5×10^{-5} per cent each of manganese and gadolinium is shown in the same figure.

Determine the contents of manganese and gadolinium in per cent, assuming that the initial activity is directly proportional to the concentration of the given components.

Solution: By extrapolating the straight portions of the decay curve to zero time, we find the logarithms of the original activity:

| | Unknown | Standard |
|----------------|---------|----------|
| Mn | | |
| $\log i_0$. . | 1.46 | 0.84 |
| i_0 | 28.9 | 7.1 |
| Cd | | |
| $\log i_0$. . | 0.98 | 0.32 |
| i_0 | 9.55 | 2.09 |

The percentage content of manganese is

$$\frac{5 \times 10^{-5} \times 28.9}{7.1} = 2.03 \times 10^{-4} \text{ per cent}$$

The percentage content of gadolinium is

$$\frac{5 \cdot 10^{-5} \times 9.55}{2.09} = 2.28 \times 10^{-4} \text{ per cent}$$

Example 5. The mass spectrum of the nitrogen produced from the air is characterized by the presence of the peaks of the isotopic forms of nitrogen $^{14}\text{N}^{14}\text{N}$ and $^{14}\text{N}^{15}\text{N}$, which are equal to 680 and 5 mm, respectively.

Determine the percentage content of nitrogen ^{15}N .

Solution: The content of nitrogen is determined by the formula

$$x = \frac{100}{2R + 1}$$

where R is the ratio of the peak heights of the isotopes of the element being determined in the mass spectrum.

$$R = \frac{h_{^{14}\text{N}}}{h_{^{15}\text{N}}} = \frac{680}{5} = 136$$

Hence

$$x = \frac{100}{2 \times 136 + 1} = \frac{100}{273} = 0.37 \text{ per cent}$$

2. PROBLEMS

SECTION A

1. The oxalates of calcium and magnesium lose water in the temperature range of 160-250 °C. In the temperature range of 450-600 °C, CaC_2O_4 is decomposed to CaCO_3 , and MgC_2O_4 to MgO , and in the interval 780-870 °C, CaCO_3 decomposes to CaO . Figure 82 shows a thermogravimetric

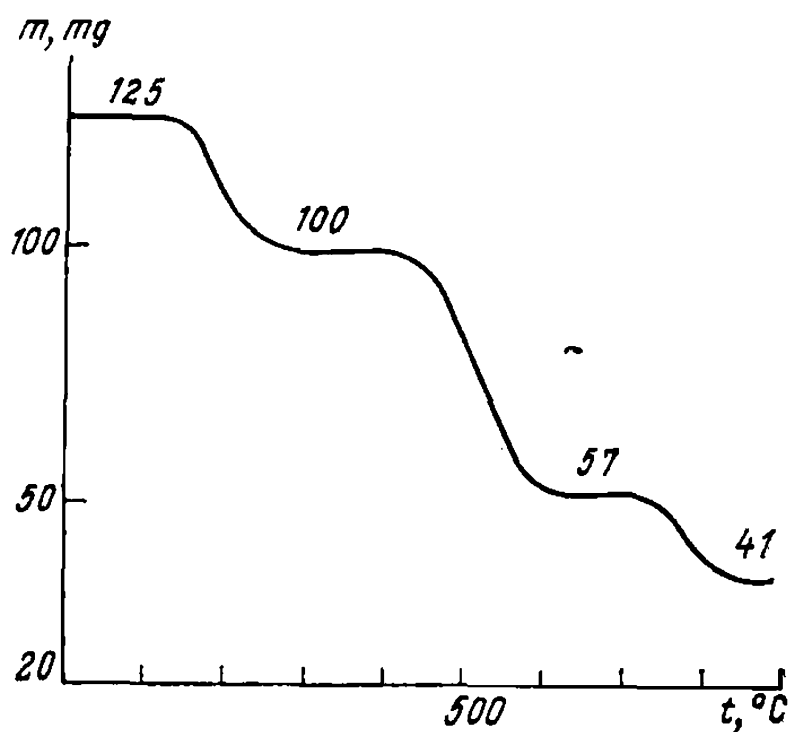


Figure 82

curve of a mixture of these products containing SiO_2 (the numbers indicate the weights for the intervals given).

Find the percentage contents of CaC_2O_4 , MgC_2O_4 , H_2O , and SiO_2 in the mixture.

2. When a mixture of gypsum, dolomite, and calcite is heated, the following processes take place: the complete dehydration of gypsum (180-200 °C), the dissociation of dolomite (720-740 °C), and the dissociation of calcite (880-920 °C).

In an analysis of the rock containing these components the loss in mass at the indicated temperature intervals was as follows: 5.2% at 180-200 °C; 5.5% at 720-740 °C; 16.3% at 880-920 °C.

Find the percentage contents of the indicated components.

3. The following processes are observed in the thermogravimetric investigation of ankerite, $\text{CaCO}_3(\text{MgFe})\text{CO}_3$: the removal of moisture (100-150 °C); the dissociation of MgCO_3 (700-770 °C); the dissociation of FeCO_3 (800-860 °C); and the dissociation of CaCO_3 (900-950 °C).

When heating a 125-mg sample of a mineral containing SiO_2 the thermogravimetric curve shown in Fig. 83 was obtained. The numbers on the curve indicate the loss in mass (in mg) in the corresponding process.

Calculate the elemental composition of the mineral being examined.

4. In a thermovolumetric analysis 200 mg of a precipitate of magnesium ammonium phosphate was heated with activated carbon to absorb NH_3 and with calcium hydride. The latter reacted with the water formed, giving an equivalent volume of hydrogen. The following volumes of hydrogen were determined under normal conditions at the temperature intervals indicated: 12.45 ml (the removal of hygroscopic water) at 80-105 °C; 102.0 ml (the removal of water of crystallization) at 105-220 °C; 8.5 ml (the removal of chemically bound water) at 220-550 °C.

Calculate the percentage contents of hygroscopic, crystallization, and chemically bound water in the precipitate. Write the formula of the compound.

5. In a thermogravimetric analysis of 100 mg of technical lime chloride the following losses in the mass are observed at various temperature intervals: 12.0 mg (the removal of hygroscopic water) at 100-130 °C; 16.3 mg (the decomposition of lime chloride with the evolution of oxygen) at 200-250 °C; 9.3 mg (the decomposition of calcium chlorate with the evolution of oxygen) at 300-330 °C; and 3.5 mg (the decomposition of calcium carbonate) at 510-590 °C.

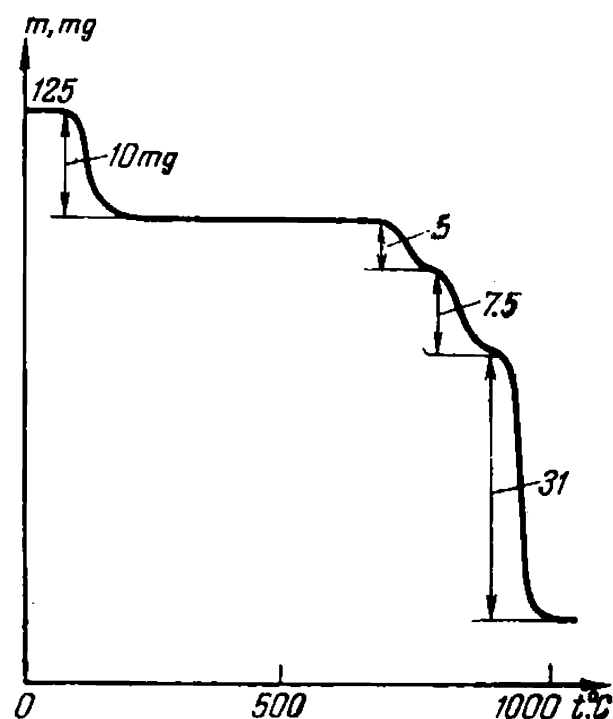


Figure 83

Find the composition of technical lime chloride, taking into account that it contains SiO_2 .

6. The mass spectrum of oxygen produced from heavy water is characterized by the presence of the peaks of the isotopic forms of oxygen $^{16}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ with wave heights of 101 and 25 mm, respectively.

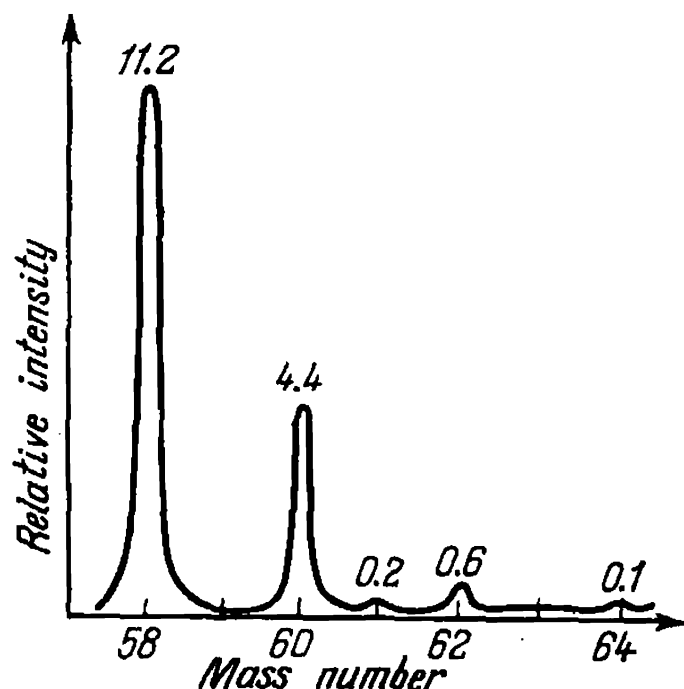


Figure 84

Determine the percentage content of oxygen ^{18}O in the mixture.

7. In the mass spectrum of a mixture of CO_2 and CH_4 there are observed lines corresponding to the following values of m/e : 8, 13, 14, 15, 16, 28, and 44.

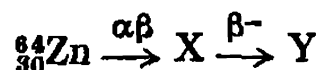
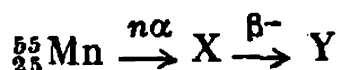
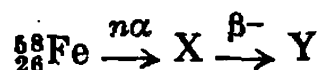
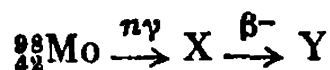
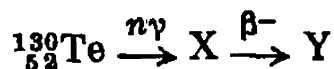
What neutral particles and positive ions might these lines correspond to?

8. From the mass-spectrum of nickel in Fig. 84 determine the atomic weight of nickel and compare it with the table value. Calculate the error of the determination if the magnitude of the signal is read with an accuracy of one-tenth.

9. Write reactions of radioactive decay and replace the letters X and Y with symbols of the elements formed:

β -decay $^{48}_{21}\text{Sc}$, $^{118}_{49}\text{In}$, $^{198}_{79}\text{Au}$

α -decay $^{233}_{92}\text{U}$, $^{252}_{98}\text{Cf}$, $^{148}_{64}\text{Gd}$



10. Samples of pure ferric oxide were irradiated with neutrons, then dissolved in hydrochloric acid, diluted to

100 ml, and evaporated to 0.2 ml, and the intensity of radiation was measured. The following results were obtained.

| | | | | |
|--|------|------|------|------|
| Sample of Fe_2O_3 , mg | 50 | 80 | 105 | 135 |
| Activity, counts per minute | 1320 | 2115 | 2740 | 3580 |

A 250-mg sample of a mineral was irradiated and dissolved in 50 ml of acid. After being evaporated under the same conditions 1 ml of this solution showed an activity of 1850 counts per minute.

Determine the percentage content of iron in the mineral.

11. A 1-g sample of an alloy containing traces of aluminium was dissolved in acid and aluminium was precipitated by 0.420 mg of Na_3PO_4 labelled with ^{32}P having an activity of 15,200 counts per minute. The activity of the precipitate formed was found to be equal to 5120 counts per minute.

Determine the percentage content of aluminium in the alloy.

12. Figure 85 is a calibration graph for determination of calcium from the intensity of gamma-radiation at 3.1 MeV.

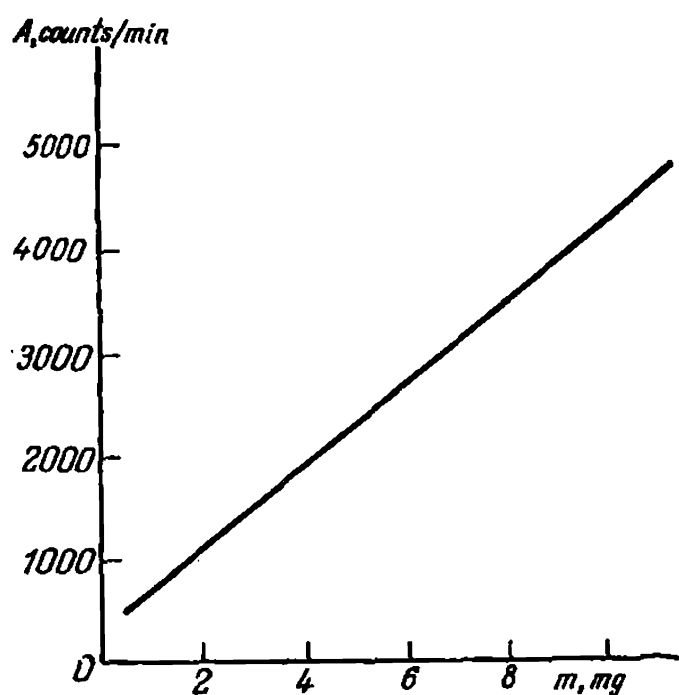


Figure 85

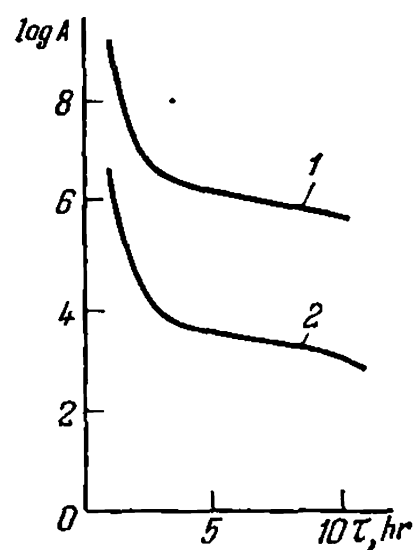


Figure 86

After irradiation a sample of a salt containing calcium carbonate and sulphate showed an intensity of gamma-radiation of 32,000 counts per 10 minutes. After treatment with

acetic acid the intensity of gamma-radiation dropped to 15,000 counts per 20 minutes.

Determine the percentage contents of calcium carbonate and sulphate in the salt.

13. To determine ^{24}Na a radioactive-decay curve was obtained for a sample containing 5 μg of sodium (see Fig. 86, curve 1).

Determine the percentage of Na in the potassium salt if the curve for 0.2 g of the salt that has been irradiated is of the form shown in Fig. 86 (curve 2).

14. A 1-g sample of copper was dissolved and after treatment the solution was diluted to 50 ml. The radiometric titration with a solution of potassium iodide in the presence of ^{204}Te as indicator gave the following results when the precipitate was removed:

| | | | | | | | |
|---|------|------|------|------|------|------|------|
| Volume of 0.05 <i>N</i> solution of KI, ml | 0 | 0.1 | 0.2 | 0.25 | 0.30 | 0.35 | 0.40 |
| Specific activity of solution, counts/ (min·ml) | 1100 | 1120 | 1090 | 880 | 640 | 450 | 220 |

Determine the percentage content of silver in the copper.

15. In the radiometric titration of a solution of silver nitrate, tagged with ^{110}Ag , by a 0.1*N* sodium chloride solution the activity of equal volumes of the solution after the addition of 2 ml of titrant and removal of the precipitate formed dropped from 1800 to 600 counts per minute.

Calculate the content of silver (in mg) in the test solution if it is known that the activity of the background is 20 counts per minute and the volume of the original solution of AgNO_3 is 5 ml.

SECTION B

16. When heating various hydrated complexes of chromium chloride the following losses in mass are observed:

(a) for yellow-violet chloride: 38.9% at 100-250 °C; 15.8% at 250-300 °C; 15.8% at 340-400 °C;

(b) for Bjerrum chloride: 15.8%* at 80-130 °C; 38.9% at 140-350 °C; 15.8%* at 350-440 °C;

(c) for green chloride: 7.8% at 60-110 °C; 15.8%* at 120-190 °C; 21.1% at 190-320 °C; 15.8%* at 320-410 °C.

The asterisk signifies that the vapours are found to contain HCl.

Set up the equations for the processes involved.

17. When a crystal hydrate of calcium dichromate is being heated, the mass is found to decrease by 10.4% at 75-80 °C and by 16.2% at 130 °C; at 440-460 °C there is observed the endothermic effect without any change in mass and at 1070-1100 °C a loss in mass of 7% is detected.

What processes take place when calcium dichromate is being heated?

18. Write equations for reactions taking place in the temperature ranges (see Fig. 87) of the thermogravimetric curve of lanthanum carbonate.

The numbers on the curve indicate the mass (in mg) at a given point.

The composition of the product (in per cent) calcined at 600 °C is as follows: La, 75.1; C, 3.3; O₂, 21.6.

19. In the thermovolumetric analysis of dolomite containing an excess of calcite, from various samples at different temperature ranges there were obtained the following volumes of CO₂ reduced to normal conditions:

| | | | | | |
|------------------------------|--------|--------|--------|--------|--------|
| Sample, g | 0.2295 | 0.2403 | 0.2150 | 0.2017 | 0.2312 |
| Volume of CO ₂ ml | | | | | |
| at 600-700 °C . . . | 28.93 | 31.73 | 27.85 | 26.40 | 30.08 |
| at 880-910 °C . . . | 30.40 | 32.55 | 29.20 | 27.47 | 30.96 |

Determine the average content of excess calcite in dolomite and $\epsilon_{0.95}$ (the 95 per cent confidence level).

20. The mass spectrum of amylacetate, CH₃COOC₅H₁₁, includes lines corresponding to the following mass numbers (m/e): 14, 28, 42, 44, 57.5, 59, 70, 71.

What particles might these lines correspond to?

21. In the mass spectrum of styrene, C₈H₅CH=CH₂, there are observed lines corresponding to the following values of m/e : 39, 50, 51, 77, 78, 103, 104.

What ions might these lines correspond to?



Figure 87

22. In the mass spectra of the olefins C_2H_4 and C_3H_6 there are observed lines corresponding to the ionized molecules and ions indicated below (relative content, in per cent):

| | | | | | | |
|---|-------------------------------|------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Radical | CH | CH ₂ | CH ₃ | C ₂ H | C ₂ H ₂ | C ₂ H ₃ |
| C ₂ H ₄ | 0.7 | 1.8 | 0.3 | 7.3 | 50 | 54.5 |
| C ₃ H ₆ | 0.3 | 0.8 | 1.7 | 0.8 | 5.8 | 24.7 |
| Radical | C ₂ H ₄ | C ₃ H | C ₃ H ₃ | C ₃ H ₄ | C ₃ H ₅ | C ₃ H ₆ |
| C ₂ H ₄ | 100 | — | — | — | — | — |
| C ₃ H ₆ | 1.2 | 9.0 | 61 | 24.7 | 100 | 69.2 |

Determine the mass spectra of these compounds.

23**. Determine the contents of the components in a gas mixture, using the mass spectra of pure components and the intensities of the lines in the mass spectrum of the mixture (see Table 42). The sensitivity coefficients S for n -butane, isobutane, propane, ethane, and methane are, respectively, 0.396, 0.464, 0.335, 0.392, 0.246.

TABLE 42

| m/e | Percentage of component | | | | | Line intensity in the spectrum of the mixture |
|-------|-------------------------|-----------|---------|--------|---------|---|
| | n -butane | isobutane | propane | ethane | methane | |
| 15 | 5.30 | 6.41 | 6.19 | 4.57 | 85.6 | 167.3 |
| 16 | 0.12 | 0.18 | 0.15 | 0.08 | 100 | 134.2 |
| 28 | 32.6 | 2.62 | 59.1 | 100 | — | 757.8 |
| 30 | 0.98 | 0.13 | 2.20 | 26.2 | — | 130.1 |
| 31 | — | — | — | 0.55 | — | 2.4 |
| 43 | 100 | 100 | 22.8 | — | — | 207.4 |
| 44 | 3.33 | 3.33 | 29.0 | — | — | 145.4 |
| 50 | 1.29 | 0.89 | — | — | — | 0.6 |
| 55 | 0.93 | 0.42 | — | — | — | 0.7 |
| 57 | 2.42 | 3.0 | — | — | — | 2.5 |
| 58 | 12.3 | 2.73 | — | — | — | 5.0 |

24. In the mass-spectrometric determination of impurities in gallium arsenide the lines were obtained for singly-charged ions with mass numbers (m/e) equal to 16, 56, and 112 and the following values of the signals, respectively, 15, 35, 48 mV. The standard sample of gallium arsenide in which these impurities were determined by chemical means and

were found to be 2×10^{-5} , 5×10^{-4} , and 3×10^{-4} per cent gave signals 10, 50 and 72 mV.

Determine the nature of these impurities and their contents in the sample (in per cent).

25**. After the irradiation of two silicon samples of equal size, one containing an unknown quantity and the other, 2×10^{-6} per cent of copper, the activity of ^{64}Cu was characterized by the following data:

| | | | | | | | | | | | |
|---|------|------|------|------|------|------|------|------|------|------|------|
| <i>E</i> , MeV | 0.48 | 0.49 | 0.50 | 0.51 | 0.52 | 0.53 | 0.54 | 0.55 | 0.56 | 0.57 | 0.58 |
| Activity of gamma- radiation, counts/min | | | | | | | | | | | |
| standard | 230 | 240 | 350 | 550 | 320 | 210 | 140 | 100 | 90 | 80 | 75 |
| unknown | 470 | 500 | 760 | 1200 | 900 | 500 | 330 | 290 | 190 | 170 | 150 |

Determine the percentage content of copper in the unknown sample from the height and area of the peak.

26. Samples of pure tin and tin-bismuth alloy of equal size were irradiated with neutrons for 30 min. Upon completion of the irradiation the activity varied with time as follows:

| | | | | | |
|-----------------------|-----|-----|-----|-----|-----|
| Irradiation time, min | 2 | 6 | 10 | 14 | 18 |
| Activity, counts/min | | | | | |
| tin | 781 | 590 | 459 | 325 | 252 |
| alloy | 340 | 247 | 205 | 145 | 121 |

Calculate the average percentage content of tin in the alloy.

27. A sample of rock of mass 25 mg, containing potassium, was characterized, after irradiation, by the following values of activity of gamma-radiation:

| | | | | | | | | | |
|--|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Irradiation period, hours | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Activity of gamma- radiation, counts/min | 1000 | 290 | 235 | 224 | 210 | 195 | 191 | 178 | 166 |

Determine the content of potassium in the mineral, using the graphs in Fig. 88 for various amounts of potassium.

28. What is the sensitivity of neutron-activation analysis in the determination of cobalt if the sample being analysed is irradiated for 10 min with slow (thermal) neutrons in a flux of 2×10^{13} neutrons per cm^2 per sec. The minimum

counting rate is 40 counts per minute at a counter efficiency of 1 per cent. During the radiation there takes place the nuclear reaction $^{59}\text{Co} (n\gamma)^{60m}\text{Co}$. The effective cross section of the reaction is $6.6 \times 10^{-25} \text{ cm}^2$.

29. Determine the content of strontium in a sample (in mg) if it is known that after the addition of 5 mg of ^{89}Sr

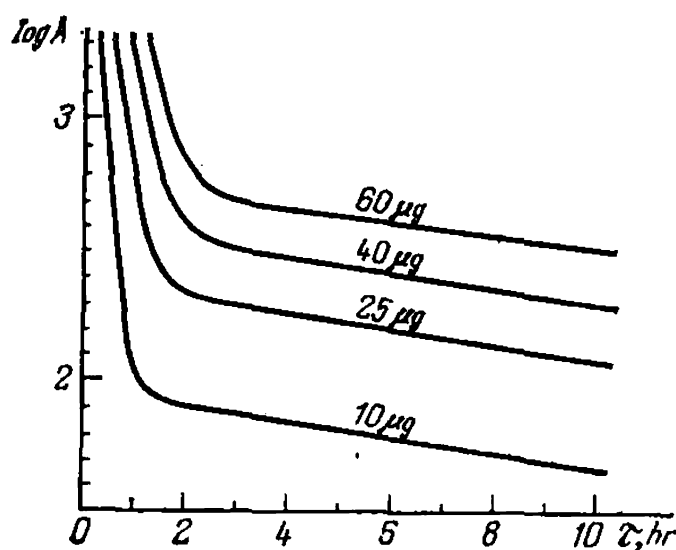


Figure 88

with a specific activity of $6.75 \times 10^{-3} \text{ } \mu\text{curie/mg}$ to the sample the activity of a strontium sample of 0.1 mg mass isolated from the sample is 50 counts per min. The counter efficiency is 0.1 %.

30. To a solution of lanthanide chlorides was added 0.1 ml of a 0.5 per cent solution (density 1.05 g/cm^3) of praseodymium chloride having an activity of 5000 counts/(min $\cdot \text{cm}^3$).

What is the content of praseodymium in the original solution if a chromatographic separation gave a sample containing 5 mg of praseodymium having an activity of 40 counts/(min $\cdot \text{mg}$).

31. To determine magnesium by radiometric titration, to identical volumes of the unknown solution, equal to 5 ml, were added various volumes of a 0.5M ammonia solution of disubstituted sodium phosphate tagged with ^{32}P . After the separation of the precipitate formed the activity of equal volumes of the solution varied, depending on the volume of titrant added, in the following manner:

| | | | | | | | |
|---------------------------------|-----|-----|-----|-----|-----|-----|-----|
| Volume of titrant, ml | 1.0 | 1.5 | 1.6 | 1.7 | 1.8 | 1.9 | 2.0 |
| Activity, counts/min | 20 | 18 | 18 | 154 | 445 | 720 | 970 |

Plot a titration curve and calculate the concentration of magnesium in the solution under study.

32. In the radiometric titration of a mixture of Zn^{2+} and Hg^{2+} in a slightly alkaline medium in the presence of $0.1 \mu\text{g}$ of ^{65}Zn as radioactive indicator with dithizone, after the extraction of dithizonates with chloroform the following values of the activity of the chloroform layer were obtained:

| | | | | | | | | | | |
|--|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Volume of 0.05N dithizone solu- tion, ml . . . | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 | 1.0 |
| Activity, counts per minute . . | 75 | 74 | 75 | 120 | 210 | 315 | 430 | 450 | 455 | 450 |

Determine the contents of Hg^{2+} and Zn^{2+} in the solution (in mg) if the titration results in the formation of complexes of the composition MeX .

33. In the radiometric determination of the solubility of SrSO_4 tagged with radioactive strontium the weighed samples indicated below were stirred for 10 hours with 100 ml of water and the activity of the solution was measured:

| | | | | | | | | | | |
|---|-----|-----|-----|------|------|------|-----|-----|-----|----|
| Weighed sample of SrSO_4 , mg | 3 | 5 | 7 | 9.5 | 10 | 10.5 | 11 | 12 | 13 | 14 |
| Activity, counts per minute | 330 | 580 | 850 | 1190 | 1260 | 780 | 520 | 300 | 140 | 80 |

Determine the solubility product of SrSO_4 and compare it with table values.

34. To determine the solubility of lead chloride, use was made of lead nitrate tagged with radioactive lead having an activity of 270 counts/(min·mg). To 10 ml of a solution containing lead nitrate with an activity of 29,500 counts per minute was added 10-fold excess of chloride ion and the precipitate was thoroughly separated. The activity of the solution was then found to decrease to 2230 counts per minute.

Determine the solubility and the solubility product of PbCl_2 and compare these values with table data.

35. To determine the efficacy of purification of GeCl_4 from AsCl_3 , the radioactive arsenic isotope ^{70}As was added to germanium tetrachloride. With the content of As being 0.35% the activity of the solution was 18,000 counts per minute. During the fractional distillation the activity of the

rectificate after the first run was 2200 counts/min and after the second run, 780 counts/min and when the distillation in the presence of copper was completed the activity dropped to 120 counts per minute.

Determine the degree of purification of germanium tetrachloride from arsenic at each stage of distillation.

36. To 150 ml of a saturated aqueous solution of iodine (the solubility of iodine in water is 0.340 g/litre) tagged with ^{131}I was added 10 ml of carbon disulphide. After the extraction the activity of the aqueous layer was found to be 84 counts/(min·ml) and that of the carbon-disulphide layer, 5×10^4 counts/(min·ml). After repeated extraction the activity of the aqueous layer became 51 counts/(min·ml) and that of the carbon-disulphide layer, 3×10^4 counts/(min·ml).

Find the iodine distribution coefficient between water and carbon disulphide and the amount of iodine left in the water after four extractions.

3. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. In which case may a minimum appear on the heating curve?

- (a) When the rate of heating is very rapid.
- (b) If there takes place an endothermic change (phase transition) or decomposition of the substance being heated.
- (c) If at a given temperature there occurs an interaction with the air oxygen.
- (d) When very large quantities of the phases being transformed are involved.

(e) No minimum can appear on the heating curve.

2. What are the advantages of the dilution method as compared with other radiochemical methods?

(a) It is faster and requires a single measurement of activity.

(b) Use may be made of substances having a very short half-life period.

(c) When this method is used, it is sufficient to know only the activity of the element being determined; no other activity measurements are needed.

(d) In distinction to other methods, it does not require the isolation of the substance being determined.

(e) It has no special advantages.

3. The mass spectrum of nitrobenzene shows the presence of particles with the following mass numbers: 30, 46, 61, 77, and 123. Which of the following sets of the products of decomposition of nitrobenzene does this mass spectrum correspond to?

(a) NO_2^+ , NO^+ , $\text{C}_6\text{H}_5\text{NO}_2^+$, C_6H_5^+ , $\text{C}_6\text{H}_5\text{NO}^+$.

(b) $\text{C}_6\text{H}_5\text{NO}_2^+$, NO_2^+ , NO^+ , C_6H_5^+ , C_6H_5^+ .

(c) $\text{C}_6\text{H}_5\text{NO}_2^+$, $\text{C}_6\text{H}_5\text{NO}_2^+$, NO^+ , NO_2^+ , C_6H_5^+ .

(d) C_6H_4^+ , NO_2^+ , NO^+ , C_6H_5^+ , $\text{C}_6\text{H}_5\text{NO}_2^+$.

(e) NO^+ , NO_2^+ , C_6H_5^+ , $\text{C}_6\text{H}_4\text{NO}^+$, $\text{C}_6\text{H}_5\text{NO}_2^+$.

4. What analytical information can be obtained with the aid of nuclear magnetic resonance (NMR)?

(a) Any element contained in the substance being analysed can be determined from the NMR spectrum.

(b) The NMR spectrum is used to determine the structure of organic molecules.

(c) The structure of all functional groups of an organic compound can be determined from the shifts of resonance frequencies in the NMR spectrum.

(d) The number and composition of the functional groups contained in an organic compound can be determined from the NMR spectrum.

(e) The shifts of the resonance frequencies in the NMR spectrum can yield data on the nature of organic groups containing protons.

5. To an unknown copper-containing sample weighing 2 g was added 25 mg of a radioactive isotope having an activity of 20,000 counts per minute. After the copper was isolated as the sulphide the activity of cuprous sulphide of 0.1 g mass was found to be 10,000 counts/min. Which of the following formulas could be used to calculate the content of copper in the sample?

$$(a) \text{ Cu, per cent} = 25 \left(\frac{\frac{20,000}{25}}{\frac{10,000}{100}} - 1 \right) \frac{100}{2000} = 8.75.$$

$$(b) \text{ Cu, per cent} = 25 \left(\frac{\frac{10,000}{100}}{\frac{20,000}{25}} + 1 \right) \frac{100}{2000} = 1.41.$$

$$(c) \text{ Cu, per cent} = 25 \left(\frac{\frac{20,000}{25}}{\frac{10,000}{10}} + 1 \right) \frac{100}{2000} = 11.3.$$

$$(d) \text{ Cu, per cent} = 25 \left(\frac{\frac{20,000}{25}}{\frac{10,000}{10}} \right) \frac{100}{2000} = 10.0.$$

(e) The data given are insufficient for calculation. The total weight of the cuprous sulphide isolated must also be known.

6. In which cases in thermogravimetric investigations could the thermal effect unassociated with the jump of the gravimetric curve be observed?

(a) When the thermal effect is associated with the evolution of gaseous products.

(b) If the thermal effect is associated with the melting of a solid.

(c) If the thermal effect is associated with the sublimation of a solid.

(d) If the thermal effect is associated with the dissociation of the substance into solid products.

(e) This phenomenon is observed in any process of dissociation.

(f) It is observed when the water of crystallization is lost.

(g) It is observed during the allotropic transformations of solids from one modification into another.

(h) This thermal effect is observed in those cases when it is very great.

7. Which of the following groups of elements are most suitable, depending on their atomic number, mass number and nuclear spin, for studies by the NMR method?

| Mass number | Atomic number | Spin |
|--------------|---------------|---------------|
| (a) $2n$ | $2n$ | 0 |
| (b) $2n$ | $2n + 1$ | An integer |
| (c) $2n + 1$ | $2n$ | $1/2(2n - 1)$ |

| | | |
|--------------|----------|----------------|
| (d) $2n$ | $2n + 1$ | $1/2 (2n + 1)$ |
| (e) $2n + 1$ | $2n + 1$ | $1/2 (2n - 1)$ |
| (f) $2n + 1$ | $2n + 1$ | 0 |
| (g) $2n$ | $2n + 1$ | 0 |

8. The isotopes of the elements given below give a γ -spectrum with energies in MeV:

| | | | | | |
|-------------------|------|------|------|------|------|
| ^{24}Mg | 0.84 | 1.02 | | | |
| ^{29}Al | 1.38 | 2.43 | | | |
| ^{59}Fe | 0.19 | 1.1 | 1.29 | | |
| ^{64}Cu | 0.51 | 1.1 | | | |
| ^{105}Ag | 0.43 | 0.51 | 0.60 | | |
| ^{117}Cd | 0.16 | 0.31 | 0.43 | 0.72 | 1.27 |
| ^{198}Au | 0.41 | 0.67 | 1.09 | | |

Indicate the answers that reflect correctly the possibilities of radioactivation determination of mixtures of these elements?

(a) Cu can be determined in the presence of Fe from the radiation of 0.51 MeV.

(b) Fe can be determined in the presence of Au from the radiation of 1.1 MeV.

(c) No radiation can be chosen for separate determination of the elements in a mixture of Fe, Ag, and Au.

(d) No radiation can be chosen for separate determination of the elements in a mixture of Cu and Ag.

(e) The elements in a mixture of Fe and Cd cannot be determined separately.

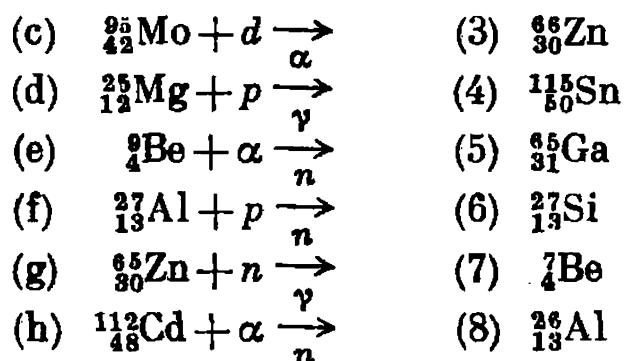
(f) In a mixture of Ag, Cd, and Au, silver can be determined from the radiation of 0.51 MeV, cadmium from any radiation, except 0.43 MeV, and gold from the radiation of 1.09 MeV.

(g) Fe interferes with the radioactivation determination of cadmium.

(h) Copper and gold can be determined only jointly from the radiation of 1.1 MeV.

9. Find under B the products of the processes of activation transformations listed under A.

| A | B |
|--|-----------------------------|
| (a) ${}^7_3\text{Li} + p \xrightarrow{n}$ | (1) ${}^{93}_{41}\text{Nb}$ |
| (b) ${}^{65}_{30}\text{Zn} + d \xrightarrow{2n}$ | (2) ${}^{12}_{12}\text{C}$ |



10. Copper and zinc can be titrated by the method of radiometric titration with the removal of the precipitate.

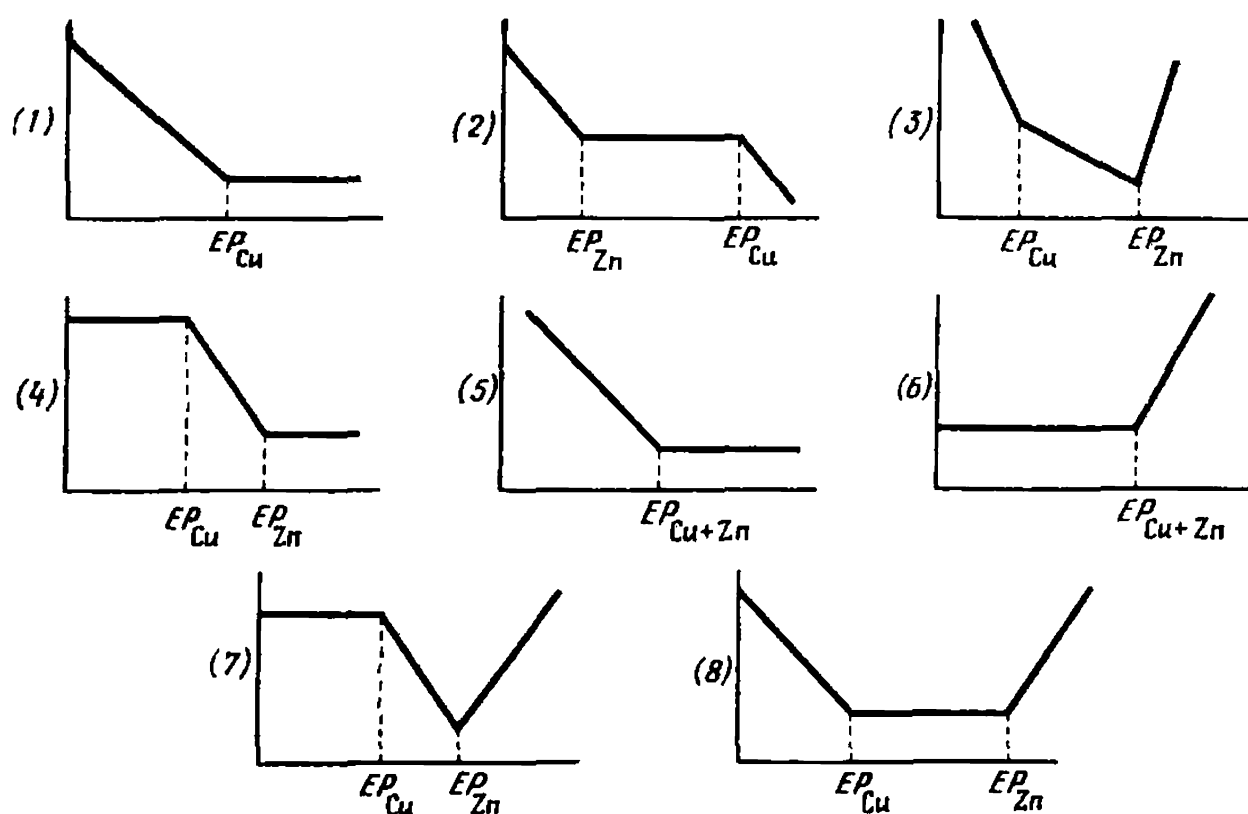


Figure 89

Assuming that $SP_{\text{Cu}_2[\text{Fe}(\text{CN})_6]} < SP_{\text{Zn}_2[\text{Fe}(\text{CN})_6]}$, find in Fig. 89 the titration curves corresponding to the conditions listed below.

| Zn^{2+} | Cu^{2+} | $\text{K}_4\text{Fe}(\text{CN})_6$ |
|------------------|------------------|------------------------------------|
| (a) active | active | inactive |
| (b) active | inactive | active |
| (c) inactive | inactive | active |
| (d) inactive | active | inactive |
| (e) inactive | active | active |
| (f) active | active | active |
| (g) active | inactive | inactive |

Physicochemical Methods of Separation

This chapter includes problems which cover extraction techniques and paper and column chromatography. Multi-variant problems are omitted and only problems of two types (A and B) are given.

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. A 100-ml volume of a solution being 0.5M with respect to FeCl_3 and 5M with respect to hydrochloric acid is shaken with 10 ml of diethyl ether. The distribution ratio for FeCl_3 in the ether-water system under these conditions is 17.6.

Determine the degree of extraction and the decrease in concentration in the aqueous phase after one extraction and the number of successive extractions required to bring the concentration of Fe^{3+} in the aqueous phase to $1 \times 10^{-4} M$.

Solution: We determine the extent of extraction and the decrease in concentration from the formulas

$$E = \frac{V_w}{1 + \frac{V_w}{V_{\text{ext}}K}}; \quad C_1 = C_0 \frac{V_w}{V_w + V_{\text{ext}}K}$$

Substituting the data given in the problem, we get

$$E = \frac{100}{1 + \frac{100}{17.6 \times 10}} = 63.5 \text{ per cent}$$

$$x_1 = 0.5 \times \frac{100}{100 + 17.6 \times 10} = 0.18 \text{ mole per litre}$$

The number of successive extractions required is determined from the equation

$$P = \frac{\log C_{in} - \log C_{fn}}{\log (V_w + V_{ext}K) - \log V_w}$$

Substituting the data given, we obtain:

$$P = \frac{\log 0.5 - \log 10^{-4}}{\log (100 + 17.6 \times 10) - \log 100} \approx 9 \text{ extractions}$$

Example 2. A 0.02*N* solution of picric acid is at equilibrium with a 0.07*N* solution of the same acid in benzene.

Determine the distribution constant of picric acid between water and benzene if its degree of dissociation in water is 0.90 and it does not dissociate in benzene. Determine the extent of extraction of picric acid from the aqueous solution after three extractions with benzene ($V_{\text{benz}} : V_w = 1 : 10$).

Solution: The distribution constant is calculated from the undissociated part of picric acid:

$$K = \frac{0.07}{0.02(1-0.9)} = \frac{0.07}{0.002} = 35$$

The content of picric acid remaining after three extractions with benzene is found by the equation given above.

Substituting the data given (the initial concentration is assumed to be equal to 100 per cent), we obtain:

$$\begin{aligned} \log C_{fn} &= \log 100 - \\ &- 3 [\log (10 + 35 \times 1) - \log 10] \\ \log C_{fn} &= 2 - \\ &- 3 (1.653 - 1) = 0.041 \end{aligned}$$

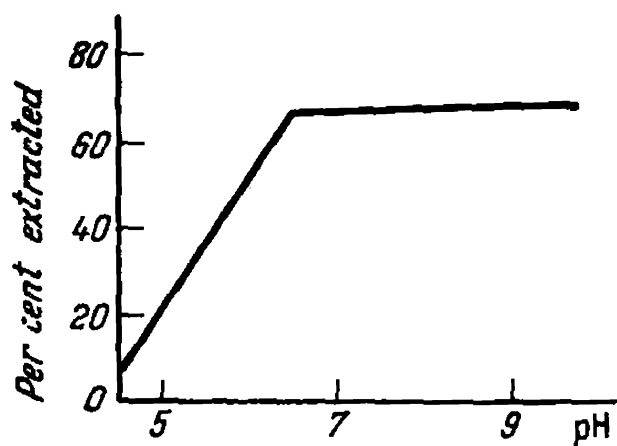


Figure 90

The extent of extraction is thus 98.88 per cent.

Example 3. An aqueous solution containing 100 mg of indium bound into a complex with bis-salicylaethylenediamine (BSEDI) is treated with an equal volume of isoamyl alcohol at $\text{pH} = 8$. The complex is then re-extracted with water at $\text{pH} = 5$.

Determine the distribution of indium in the three solutions indicated after extraction and re-extraction, using the graph given in Fig. 90.

Solution: In an extraction with isoamyl alcohol, 65 per cent of the indium complex is extracted. Hence, 35 mg is left in the aqueous phase, and 65 mg, in the isoamyl alcohol.

In re-extraction 17 per cent is left in isoamyl alcohol and 83 per cent is re-extracted into the aqueous phase. Hence, the content of indium in isoamyl alcohol will be $(65 \times 17)/100 = 11$ mg and that in the aqueous phase, 54 mg.

Example 4. To 100 ml of 0.1*N* hydrochloric acid was added 5 grams of a cation-exchange resin (or cation-exchanger) in the Na^+ form. When the equilibrium was reached, the hydrogen ion concentration decreased to 0.015*N*.

Determine the static exchange capacity for hydrogen ions.

Solution: We determine the number of gram-equivalents of H^+ that have been adsorbed by the cation-exchanger:

$$n = \frac{(0.1 - 0.015) 100}{1000} = 0.0085 \text{ g-eq} = 8.5 \text{ mg-eq}$$

Hence the static exchange capacity will be equal to

$$K = \frac{8.5}{5} = 1.7 \text{ mg-eq/g}$$

Example 5. To determine the dynamic capacity of a cation-exchange resin, 500 ml of a 0.05*N* solution of calcium was passed through a column containing 5 grams of the cation-exchanger. In the determination of calcium in the eluate in 50-ml portions the following values of concentration were obtained: 0.003, 0.008, 0.015, 0.025, 0.040, 0.050, and 0.050.

Determine the dynamic capacity of the cation-exchanger for calcium.

Solution: We calculate the number of milligram-equivalents of Ca adsorbed from each portion of the eluate:

$$\text{I. } \frac{(0.050 - 0.003) 50}{1000} = 0.00235 \text{ g-eq} = 2.35 \text{ mg-eq.}$$

$$\text{II. } \frac{(0.050 - 0.008) 50}{1000} = 2.1 \text{ mg-eq.}$$

$$\text{III. } \frac{(0.050 - 0.015) 50}{1000} = 1.75 \text{ mg-eq.}$$

$$\text{IV. } \frac{(0.050 - 0.025) 50}{1000} = 1.25 \text{ mg-eq.}$$

$$\text{V. } \frac{(0.050 - 0.040) 50}{1000} = 0.50 \text{ mg-eq.}$$

$$\text{VI. } 0 \text{ mg-eq.}$$

The amount adsorbed is

$$2.35 + 2.10 + 1.75 + 1.25 + 0.50 = 7.95 \text{ mg-eq}$$

Hence the dynamic capacity is

$$K = \frac{7.95}{5} = 1.59 \text{ mg-eq/g}$$

Example 6. In the determination of furfural in a mixture by a gas-chromatographic method the area of its peak S_{fur} was compared with the area of the peak of *o*-xylene, S_{xyl} , which was introduced as a standard. The following peak areas were obtained.

For the standard containing 25 per cent of furfural, $S_{\text{xyl}} = 25 \text{ mm}^2$ and $S_{\text{fur}} = 11 \text{ mm}^2$.

For the unknown sample, $S_{\text{xyl}} = 22 \text{ mm}^2$ and $S_{\text{fur}} = 18.5 \text{ mm}^2$.

Determine the content of furfural in the unknown sample.

Solution: The concentration in the mixture is proportional to the ratio of the peak areas:

$$\frac{C_{\text{st}}}{C_x} = \frac{\left(\frac{S_{\text{fur}}}{S_{\text{xyl}}} \right)_{\text{st}}}{\left(\frac{S_{\text{fur}}}{S_{\text{xyl}}} \right)_x}$$

Substituting the data of the problem, we obtain:

$$\frac{25}{C_x} = \frac{\frac{11}{25}}{\frac{18.5}{22}}; \quad C_x = \frac{25 \times 18.5 \times 25}{22 \times 11} = 47.5 \text{ per cent}$$

2. PROBLEMS

SECTION A

1. Calculate the degree of extraction of a complex with benzene from an aqueous solution if the initial concentration of the complex is 0.0025 mole per litre and its content in benzene is 0.040 mole per litre. The ratio of the volumes of the organic and aqueous phases in the process of extraction is 1 : 20.

2. Determine the degree of extraction of nickel dimethylglyoximate from 50 ml of aqueous solution at $\text{pH} = 8$ after being shaken twice with 5 ml of chloroform. The distribution coefficient is $K = 410$.

3. A coloured complex of a concentration of 0.001 mole per litre having an optical density of 0.65 with a layer thickness of 10 mm was extracted with amylacetate, the distribution coefficient of which with respect to acidulated aqueous solution is $K = 99$.

What will be the optical density of the aqueous solution after one extraction with amyl alcohol ($V_{\text{al}} : V_{\text{w}} = 1 : 10$) and the optical density of the extract after tenfold dilution if the molar extinction coefficient (molar absorptivity) does not change?

4. Lanthanum, samarium and thorium are extracted in the form of hydroxyquinolates from 100 ml of aqueous 0.1M salt solutions by three successive extractions with chloroform.

Calculate the minimum volume of solvent required for unit extraction of each of these elements in order to reduce their concentration in aqueous solution to 1×10^{-4} mole/litre. The distribution coefficients, or ratios, are, respectively, equal to $K_{\text{La}} = 370$, $K_{\text{Sm}} = 280$, and $K_{\text{Th}} = 250$.

5. To determine the exchange capacity of espatite in the form of Ca^{2+} , to 2 grams of espatite was added 25 ml of a 0.1N solution of NaOH. When the equilibrium was reached, the solution was titrated with 0.08N hydrochloric acid. A 15.7-ml volume of the acid was used up for the titration.

Determine the exchange capacity of espatite.

6. How many grams of nickel will remain in the solution if 500 ml of a 0.05N nickel salt solution was passed through

a column filled with 10 grams of a cation-exchange resin. The total dynamic capacity under the given conditions of separation is 1.4 mg-eq/g.

7. Through a column filled with 5 g of a cation-exchanger was passed 500 ml of a copper solution. The effluent 50-ml portions of the solution were titrated iodometrically. The first two portions contained no copper. The titration of the 3d, 4th, 5th, 6th, 7th, 8th, 9th, and 10th portions required the use of 5, 12, 17.6, 20, 26.2, 30.5, 39.2 and 39.22 ml of a 0.02*N* sodium thiosulphate solution, respectively.

Plot a graph of copper concentration versus volume of eluate. Calculate the total dynamic capacity and the dynamic capacity.

8. When running a polarogram on 10 ml of a copper solution a wave with a height of 55 mm was obtained; after the addition of 1 ml of a standard copper-containing solution with a concentration of 1 mg/ml the wave height increased to 59.5 mm. After the treatment of 200 ml of a solution of 5 grams of a cation-exchanger the height of the polarographic wave of copper obtained in the analysis of 10 ml of the solution became 5.5 mm, and after adding the same standard solution the wave height increased to 30 mm.

Determine the exchange capacity of the cation-exchanger.

9. To determine nickel in ferrites by paper chromatography, the following spot areas on a strip of filter paper impregnated with dimethylglyoxime with water as solvent were obtained depending on the concentration of nickel?

| | | | | | | |
|----------------------------|-----------|------|------|------|------|------|
| <i>C</i> , mg/0.2 ml | | 0.12 | 0.45 | 0.90 | 1.20 | 1.65 |
| <i>S</i> , mm ² | | 26 | 44 | 66.5 | 83 | 105 |

When analysing ferrite its sample weighing 500 mg was dissolved in acids and diluted to 25 ml. A volume of 0.20 ml of the solution was pipetted onto a strip of filter paper and after chromatographic separation the spot area was determined, which was found to be equal to 52.5 mm².

Determine the percentage content of nickel in the ferrite.

10. On the basis of the values of *R_f* given below for two solvents plot a two-dimensional chromatogram. Which of the substances indicated cannot be separated by one-dimensional chromatography using two solvents? Which substances cannot be separated by two-dimensional chromatography?

| | Ethylaceta- te-water- acetic acid | Ethylaceta- te-formami- de-pyridine |
|------------------------------------|---|---|
| Glycero-1-phosphate | 0.80 | 0.54 |
| Glycero-2-phosphate | 0.82 | 0.23 |
| Fructose-6-phosphate | 0.54 | 0.54 |
| Ribose-1-phosphate | 0.47 | 0.50 |
| Glucose-1-phosphate | 0.44 | 0.44 |
| Glucose-6-phosphate | 0.36 | 0.50 |
| Glycero-2,3-diphosphate | 0.33 | 0.15 |
| Fructose-1,6-diphosphate | 0.24 | 0.13 |

11. In studying the chromatograms of mixtures of chloromethylphosphinic acids tagged with ^{32}P a radiochromatogram was obtained, for 10 mg of their mixture, of the portion from 10 to 20 cm with spots of various acids. The activity of radiation for this portion is given in Fig. 91a.

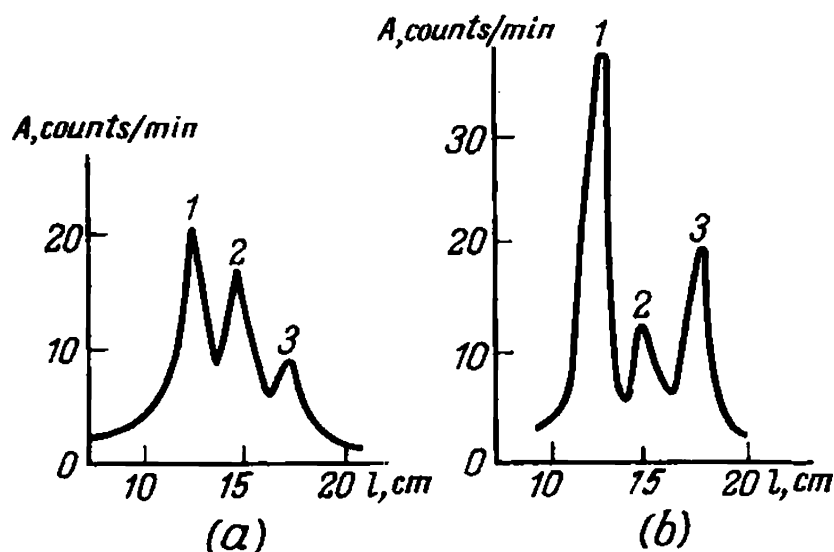


Figure 91

For the unknown sample there was obtained a second chromatogram, the one shown in Fig. 91b. The peaks correspond to: 1— $\text{CH}_2\text{ClPO}_3\text{H}_2$; 2— $\text{CHCl}_2\text{PO}_3\text{H}_2$; 3— $\text{CCl}_3\text{PO}_3\text{H}_2$.

Find the content (in mg) of chlorophosphoderivatives in the unknown sample, assuming that the number of counts is proportional to the concentration.

12. In determining ethyl alcohol by gas chromatography the following peaks were obtained depending on the content:

| | | | | | |
|--------------------|-----|-----|-----|-----|-----|
| C , mg | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
| h , mm | 18 | 37 | 48 | 66 | 83 |

For 0.02 ml of the unknown solution a peak was obtained with a height of 57 mm.

Determine the percentage content of the alcohol in the unknown solution if the density of the solution is 0.95 g/cm³.

SECTION B

13**. The distribution of phenol (in moles per litre) between water and benzene is characterized by the following data:

| | | | | | |
|-------|-----------|-------|-------|------|------|
| C_w | | 0.032 | 0.12 | 0.33 | 0.75 |
| C_b | | 0.077 | 0.016 | 0.25 | 0.39 |

Calculate K and n in the distribution equation:

$$K = \frac{C_b^n}{C_w}$$

How will the concentration of a 0.2M solution of phenol change after treatment with an equal volume of benzene?

14. To determine traces of iron, a sample weighing 9.9750 grams was dissolved in 150 ml and the iron was converted to nitrosonaphthalate. Then, after its 10-ml portions were extracted with isoamyl alcohol by two successive extractions (the extent of extraction being 95 per cent), the combined extracts were diluted with alcohol to 25 ml and examined photometrically on a spectrophotometer at 700 nm. The optical density of the resulting extract measured relative to the extract obtained in a blank experiment is 0.325 at $l = 5$ cm. The molar absorptivity of iron nitrosonaphthalate of the composition FeX_2 in isoamyl alcohol is $\epsilon = 45,000$.

Find the percentage content of iron in the sample.

15. To determine cobalt, two 10-ml portions of cobalt hydroxyquinolate were successively extracted at $\text{pH} = 7$ with isoamyl alcohol from 100 ml of 0.01N aqueous solution. The combined extract was treated twice with equal volumes of acidulated water at $\text{pH} = 2$.

Find the concentration of cobalt in the combined re-extract and the loss of cobalt during re-extraction, using the graph of Fig. 92 representing the logarithm of the distribution

coefficient of cobalt hydroxyquinolate between water and isoamyl alcohol versus pH.

16. A volume of 100 ml of acetylacetone containing 80 mg of beryllium as acetylacetonate was shaken with 100 ml of acidulated water until an equilibrium was set up. The aqueous layer was then separated and the beryllium concentration in it was found to be 0.05 mg/ml. How many successive unit extractions would be necessary to remove beryllium by acetylacetonate from the aqueous phase to reduce its concentration 1000 times.

17. Calculate the extent of extraction of copper from 500 ml of a 0.002*N* solution of $\text{Cu}(\text{NO}_3)_2$ with permutite if the titration of the copper isolated from the coloured zone with 50 ml of a 5 per cent hydrochloric acid used up 7.5 ml of a 0.06*N* sodium thiosulphate solution in the iodometric determination of copper.

18. A 1.095-g sample of beryllium bronze containing Be and Cu was dissolved and the resulting solution was diluted with water to 50 ml. The solution was passed through a column with 5 grams of a cation-exchanger, whose exchange capacity was 3.2 mg-eq/g. The effluent solution was found to contain 3 mg of copper.

Determine the extent to which beryllium and copper were separated from each other in the column (beryllium is not retained by the cation-exchanger).

19. In the determination of adipic acid in the product of butadiene hydrocarboxylation by paper chromatography the spots developed with methyl red were cut out, dried and weighed. For artificial mixtures the following data were obtained at various contents of adipic acid:

| | | | | | |
|--|----|-----|-----|-----|-----|
| Content of acid, μg | 5 | 10 | 15 | 20 | 25 |
| Mass of stained paper, mg | 78 | 123 | 154 | 172 | 194 |

A 100-mg sample of the product being analysed was dissolved in 10 ml of water and three 0.02-ml portions of the resulting solution were analysed chromatographically. The

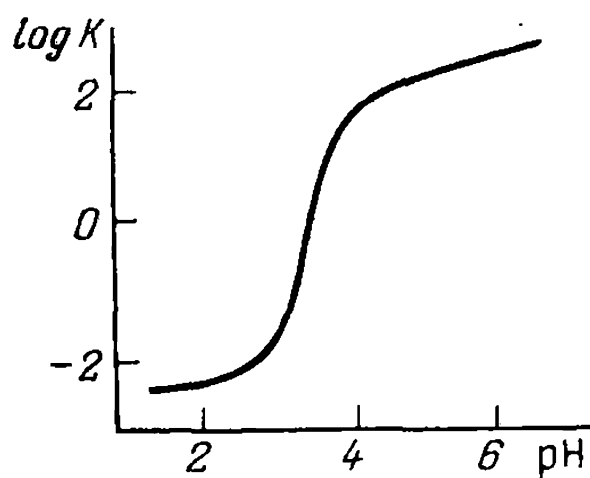


Figure 92

spots obtained were found to have masses of 105, 98, and 109 mg.

Find the average percentage content of adipic acid in the product being analysed and the error of the determination.

20. A 0.750-g sample of a natural product was dissolved in 100 ml of alcohol and 0.05 ml of the alcohol solution was applied to a strip of filter paper. The spots of uridylic acid, $C_9H_{11}O_5N_2(OPO_3H_2)$, riboso-1,5-diphosphate, $C_9H_{10}O_3(OPO_3H_2)_2$, and adenylic acid, $C_{15}H_{18}O_3N_5OP(OC_7H_7)_2$ obtained were cut out and fused with KOH and $K_2S_2O_8$ and after the alloy was dissolved the phosphorus was determined photometrically. The values of the optical density obtained were, respectively, 0.43, 0.62, and 0.18. A standard phosphorus solution with a concentration of phosphorus of 0.2 $\mu\text{g/ml}$ gave a solution having an optical density of 0.85.

Determine the per cent concentrations of these derivatives in the natural product.

21. Figure 93 shows a graph for quantitative determination of *cis*-1,2-dichloroethylene in vinylidene chloride by gas chromatography. The peak of toluene was used as the reference peak. The following data were obtained in the analysis of three production samples:

| Sample | I | II | III |
|--|----|----|-----|
| Peak of <i>cis</i> -1,2-dichloroethylene | | | |
| base | 8 | 4 | 12 |
| height | 35 | 12 | 60 |
| Peak of toluene | | | |
| base | 10 | 8 | 10 |
| height | 52 | 45 | 50 |

Determine the percentage content of *cis*-1,2-dichloroethylene in a mixture of these samples with a ratio of 1 : 1 : 3.

22. To determine impurities in helium by gas chromatography a calibration graph was constructed for standard samples (shown in Fig. 94). When the peak areas were determined for two samples with a planimeter, the following readings were obtained on the planimeter scale with 1 litre of helium being passed:

| Peak | O ₂ | H ₂ | N ₂ |
|----------------------|----------------|----------------|----------------|
| 1st sample | 3.40 | 0.80 | 2.20 |
| 2nd sample | 1.90 | 0.60 | 1.70 |

The average value of the reading on the planimeter scale for 1 cm^2 was 0.80.

Determine the percentage content of the gases in the samples. How will this content change after the catalytic burning-up of hydrogen and condensation of water vapours?

23. To determine dioxydiphenylmethane in foodstuffs use is made of the method of thin-layer chromatographic separation and quantitative determination from the spot area S

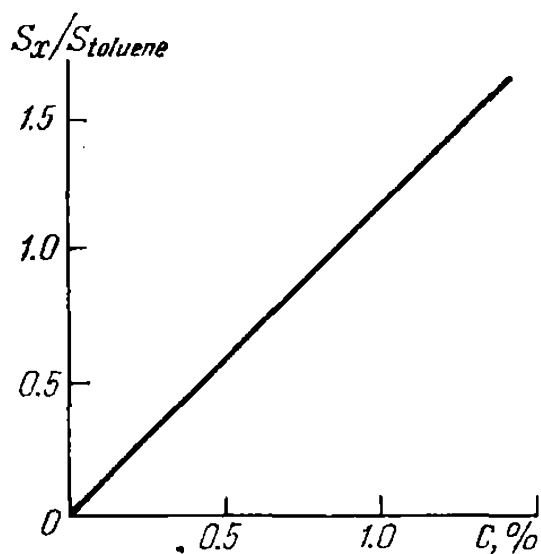


Figure 93

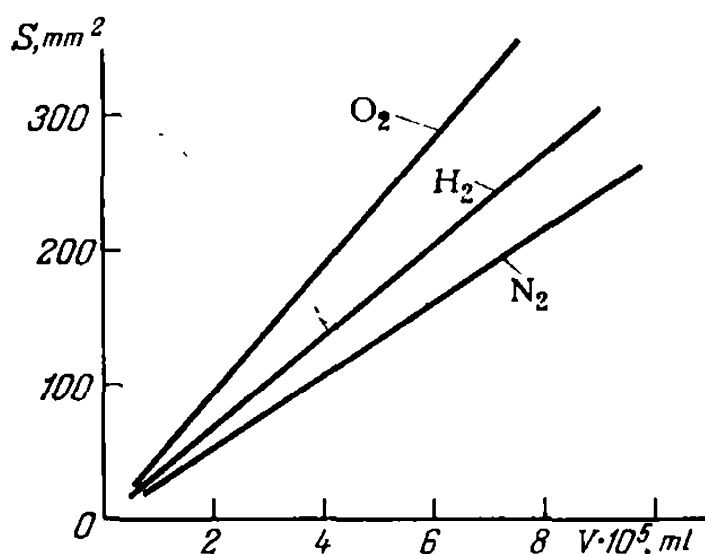


Figure 94

and the intensity of reflection photocurrent I . The following data were obtained for two standards:

| | | | | | | |
|--|------|------|------|------|------|------|
| Concentration of dioxydiphenylmethane, $\mu\text{g}/0.02 \text{ ml}$ | 1.25 | 2.56 | 6.40 | 18.2 | 33.1 | 77.3 |
| Spot area, mm^2 | 9 | 17 | 29 | 55 | 80 | 120 |
| Intensity of reflection photocurrent, mA | 2.3 | 2.8 | 3.4 | 4.3 | 5.1 | 7.2 |

To plot a calibration graph the relation between $\log S \cdot I$ and $\log C$ was used.

150 grams of vegetables were treated with 100 ml of alcohol, which was then evaporated to 10 ml. From 0.02 ml of this solution a spot was obtained, in a chromatographic analysis, with an area of 35 mm^2 , the intensity of reflection photocurrent being 2.5 mA.

Determine the content of dioxyphenylmethane in the vegetables (in $\mu\text{g}/\text{kg}$).

3. ASSIGNMENTS FOR PROGRAMMED QUESTIONING

1. In which cases is re-extraction resorted to for analytical purposes?

(a) Re-extraction is used to intensify the colour of the substance being determined.

(b) Re-extraction is resorted to in those cases when the determination of a substance in an organic phase is impeded by some circumstances.

(c) Re-extraction is used to convert the substance under study into the ionic state.

(d) Re-extraction is used to concentrate the substance being determined.

(e) Re-extraction is resorted to in those cases when the colour of the organic phase is too intense.

2. What substances can be determined by gas chromatography depending on the state of aggregation?

(a) Any gaseous substance.

(b) Any substance that at temperatures up to 100 °C is converted into the gaseous state.

(c) Any gases and liquids.

(d) Any gaseous substances, low-boiling liquids, and readily evaporating solids.

(e) The possibility of determination by this method does not depend on the state of aggregation.

3. To 250 ml of a solution containing 0.5 g of zinc chloride (molecular weight 136) was added 5 g of a cation-exchanger. After the equilibrium was set up the content of zinc chloride was found to be 0.050 g. Which of the following formulas should be used to determine the static exchange capacity of the cation-exchanger with respect to zinc ions?

$$(a) \frac{(0.500 - 0.050)}{5} = 0.090.$$

$$(b) (0.500 - 0.050) \frac{65.3}{136} = 0.216.$$

$$(c) \frac{(0.500 - 0.050)}{5} \times \frac{65.3 \times 1000}{136} = 43.2.$$

$$(d) \frac{(0.500 - 0.050)}{5} \times \frac{65.3}{136} = 0.0432.$$

(e) The data given are insufficient for calculation. It is necessary to know the specific gravity of the solution.

4. A 25-ml volume of methyl isobutyl ketone is used to extract Mo^{VI} from 200 ml of 4*M* hydrochloric acid. The distribution coefficient is equal to $E = 10$. Which of the following formulas could be used to calculate the residual concentration of molybdenum after three unit extractions if the initial concentration is 100 $\mu\text{g/ml}$?

$$(a) \quad C = \frac{100}{\left(1 + \frac{10}{200/25}\right)^3} = 8.8 \mu\text{g/ml}.$$

$$(b) \quad C = \frac{100}{\left(1 + \frac{10}{25/200}\right)^3} = 1.9 \times 10^{-4} \mu\text{g/ml}.$$

$$(c) \quad C = \frac{100}{10} \left(\frac{25}{200}\right)^3 = 1.8 \times 10^{-2} \mu\text{g/ml}.$$

$$(d) \quad C = \frac{100}{(1+10)^3} \left(\frac{200}{25}\right)^3 = 41 \mu\text{g/ml}.$$

(e) The data given are insufficient for calculation.

5. Figure 95 shows the curves for the extraction of hydroxyquinolates of three metals depending on pH. Indicate

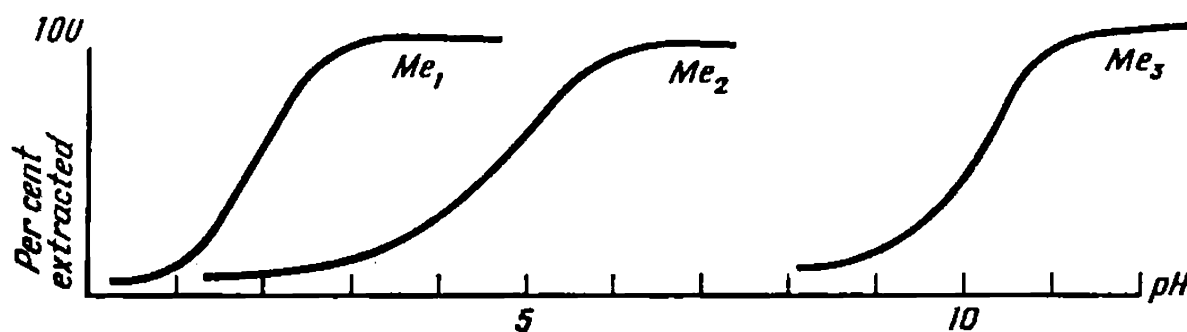


Figure 95

the answers that would characterize correctly the possibility of extractive separation of these metals.

(a) All the three metals can be separated by controlling the pH of extraction and re-extraction.

(b) Me_3 can be separated from Me_1 and Me_2 by extraction at $\text{pH} = 13$ and re-extraction of the organic phase at $\text{pH} = 8$.

(c) Me_2 can be separated from Me_1 by extracting at $\text{pH} = 7$ and re-extracting the organic phase at $\text{pH} = 3$.

(d) Me_2 cannot be separated from Me_3 by extraction.

(e) Me_1 and Me_3 can be isolated from the solution separately by carrying out extraction in a weakly acidic medium for the first metal and in ammonia buffer for the second.

(f) It is not reasonable to extract Me_1 and Me_2 at $\text{pH} = 8$ and re-extract Me_2 at $\text{pH} = 4$ (it would be a gross error to do this) since the metal would be re-extracted incompletely.

(g) To choose conditions for separation of these metals by extraction is impossible.

6. Indicate under A the organic groupings characteristic of cation-exchangers, and under B those for anion-exchangers.

- | A | B |
|---|---|
| (a) $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ | (1) $=\text{C}=\text{O}$ |
| (b) $=\text{NH}$ | (2) $-\text{CH}_3$ |
| (c) $-\text{CH}_3$ | (3) $=\text{NH}$ |
| (d) $=\text{S}$ | (4) $-\text{N}(\text{CH}_3)_3$ |
| (e) $-\text{S} \begin{smallmatrix} \nearrow \text{OH} \\ \searrow \text{O} \\ \parallel \text{O} \end{smallmatrix}$ | (5) $-\text{OH}$ |
| (f) $=\text{C}=\text{O}$ | (6) $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}$ |
| (g) $-\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$ | (7) $\equiv \text{N}$ |
| (h) $-\text{OH}$ | (8) $-\text{NH}_2$ |

7. Find under B the characteristics of the chromatographic methods listed under A.

A

- (a) Radial chromatography.
- (b) Thin-layer chromatography.
- (c) Ascending chromatography.

- (d) Two-dimensional chromatography.
- (e) Descending chromatography.
- (f) Precipitation chromatography.

B

(1) In this method, two different solvents are used for separation and the elution is carried out in mutually perpendicular directions.

(2) In this method, the procedure is accomplished in a thin layer of a solvent.

(3) In this method, the adsorbent is subjected to preliminary treatment with reagents that form precipitates with the substances being determined.

(4) In this method, the solvent climbs up a strip of filter paper by capillarity.

(5) In this method, the separation is accomplished successively by treating chromatograms with two solvents.

(6) In this method, the substance under study and the solvent are placed in the centre of a circle and the development is carried out by sectors.

(7) In this method, the solvent is made to move by gravity and capillarity.

(8) In this method, use is made of adsorbents that react with the substances being determined to form precipitates.

(9) In this method, the separation is effected in a thin layer of an adsorbent.

(10) In this method, an ascending chromatogram is obtained with one solvent, and then a descending one with another.

8. Find under B the definitions of the basic concepts (listed under A) used in extraction methods.

A

- (a) The extraction constant.
- (b) The partition constant (distribution constant).
- (c) The distribution (partition) ratio.
- (d) The extent of extraction.
- (e) The separation factor.

B

(1) The percentage of the substance extracted under given conditions into an organic phase.

(2) Under equilibrium conditions it is the ratio of the concentration of a definite form of a substance in the organic phase to the concentration of the same form in the aqueous phase.

(3) It is the equilibrium constant of the process of extraction.

(4) Under equilibrium conditions it is the ratio of the total analytical concentration of a substance in the organic phase to the total analytical concentration of the substance in the aqueous phase.

(5) It is the ratio of the distribution coefficients of the substances being separated.

9. Find under B the characteristics of the detectors (listed under A) used in gas chromatography.

A

- (a) Ionization detector.
- (b) Thermochemical detector.
- (c) Flame-ionization detector.
- (d) Electron-capture detector.
- (e) Integral detector.
- (f) Flame detector.

B

(1) This detector measures the flame temperature in the burning of organic substances and hydrogen.

(2) The total amount of gas passed is determined from the total volume or other parameters.

(3) In this detector, the substances passed are ionized by radioactive radiation, which affects the electrical conductance of the gas.

(4) This detector measures the change in the ionization current arising from the absorption of electrons by organic particles.

(5) This detector measures the change in the ionization current arising as a result of the formation of charged particles in the flame.

(6) This detector measures the heat of the catalytic burning of organic compounds in the carrier gas.

10. Figure 96 shows the curves for the elution of 4 substances, A, B, C, and D, out of the ion-exchange column as

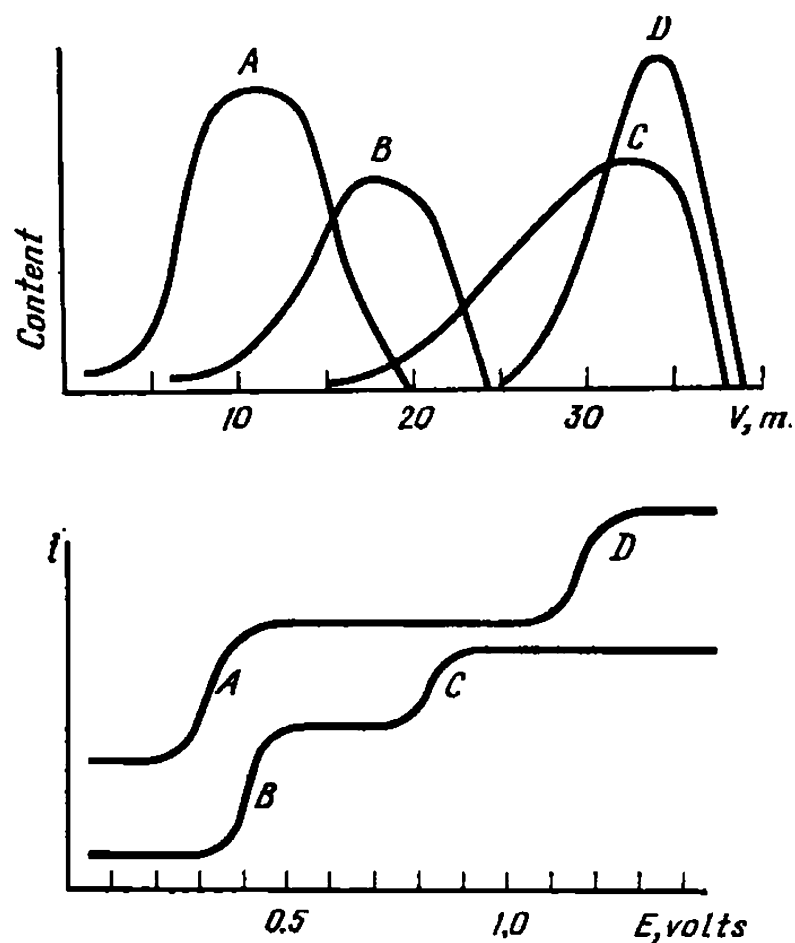


Figure 96

a function of the eluate volume. The polarograms of these substances are also given.

Find under A the correct answer as to the possibility of separation and polarographic determination of a mixture of these substances and under B the conditions for this determination.

A

(a) All the four substances can be isolated and determined separately.

(b) The substances A and B mutually interfere with their separation and determination, C and D are eluted together but do not interfere with each other.

(c) When B is eluted, C is also partially eluted together with it and interferes with the determination of B.

(d) The substances A and B can be eluted and determined separately, and C and D are eluted and determined together.

(e) Neither of the substances indicated can be determined separately.

B

(1) The substance A is determined in the first portion of the eluate having a volume of up to 10 ml; B is determined in the portion from 10 to 17.5 ml, and C and D are determined together in the portion from 17.5 to 32.5 ml.

(2) A portion of eluate from 0 to 25 ml is taken and A and B are determined together in it, and in a portion from 25 to 35 ml C and D are determined separately.

(3) A portion of eluate from 0 to 25 ml is taken and A and B are determined together in it at a potential of 0.3-0.4 V, and at a potential of 0.8-0.9 V traces of eluted C are determined. Then, in the second portion of eluate from 25 to 35 ml, at a potential of 0.8-0.9 V, there is determined the bulk of C, to which is added the amount found previously, and at a potential of 1.2-1.3 V the content of D is determined.

(4) A portion of eluate from 0 to 15 ml is taken and at a potential of 0.3-0.4 V the substance A is determined; in the second portion, from 15 to 25 ml, the substance B is determined at the same potential. The errors in the determinations of A and B due to the presence of impurities of B and A, respectively, compensate each other. In the third portion, from 25 to 35 ml, at a potential of 1.2-1.3 V the total content of C and D is found.

(5) No conditions for separate determination of any of these substances can be chosen.

Kinetic Methods of Analysis and Combination Problems

This chapter includes problems covering various methods of physicochemical analysis in combination with physicochemical methods of separation and some problems on kinetic methods of analysis.

1. EXAMPLES OF PROBLEM-SOLVING

Example 1. To determine traces of copper the reaction between H_2O_2 and *p*-phenetidine (ethoxyaniline) is used, which proceeds with the formation of coloured products and is catalysed with copper salts. For quantitative determination there has been studied the variation of the optical density of a solution with time in the presence of various amounts of copper:

| Concentration of Cu, $\mu\text{g/ml}$ | 0 | 0.0015 | 0.0030 | 0.0050 | 0.0075 |
|---------------------------------------|------|--------|--------|--------|--------|
| Optical density after | | | | | |
| 1 min | 0 | 0.05 | 0.09 | 0.11 | 0.17 |
| 2 min | 0.02 | 0.07 | 0.13 | 0.21 | 0.30 |
| 3 min | 0.03 | 0.12 | 0.21 | 0.34 | 0.43 |
| 4 min | 0.05 | 0.18 | 0.28 | 0.43 | 0.58 |
| 5 min | 0.04 | 0.19 | 0.36 | 0.53 | 0.76 |

The following values of optical density were found for a solution with an unknown content of copper under the same conditions:

| | | | | | |
|------------------------|------|------|------|------|------|
| τ , min | 1 | 2 | 3 | 4 | 5 |
| D | 0.09 | 0.17 | 0.29 | 0.35 | 0.45 |

Determine the concentration of the unknown solution.

Solution: From the data given we plot a graph representing the optical density versus time (Fig. 97a) and determine the slopes of the straight lines obtained:

| | | | | | |
|--|------|--------|--------|--------|--------|
| C_{Cu} , $\mu\text{g/ml}$ | 0 | 0.0015 | 0.0030 | 0.0050 | 0.0075 |
| $\tan \alpha$ | 0.05 | 0.20 | 0.35 | 0.54 | 0.74 |

Now we construct a graph of $\tan \alpha$ against the concentration of copper (see Fig. 97b). Next we plot a graph representing optical density D versus time for the solution with an unknown amount of copper and determine the slope of this straight line: $\tan \alpha = 0.45$. From the second graph we find the concentration, which is $0.0043 \mu\text{g/ml}$.

Example 2. The reaction of reduction of nickel ion to the metal by hypophosphite is catalyzed by platinum ions.

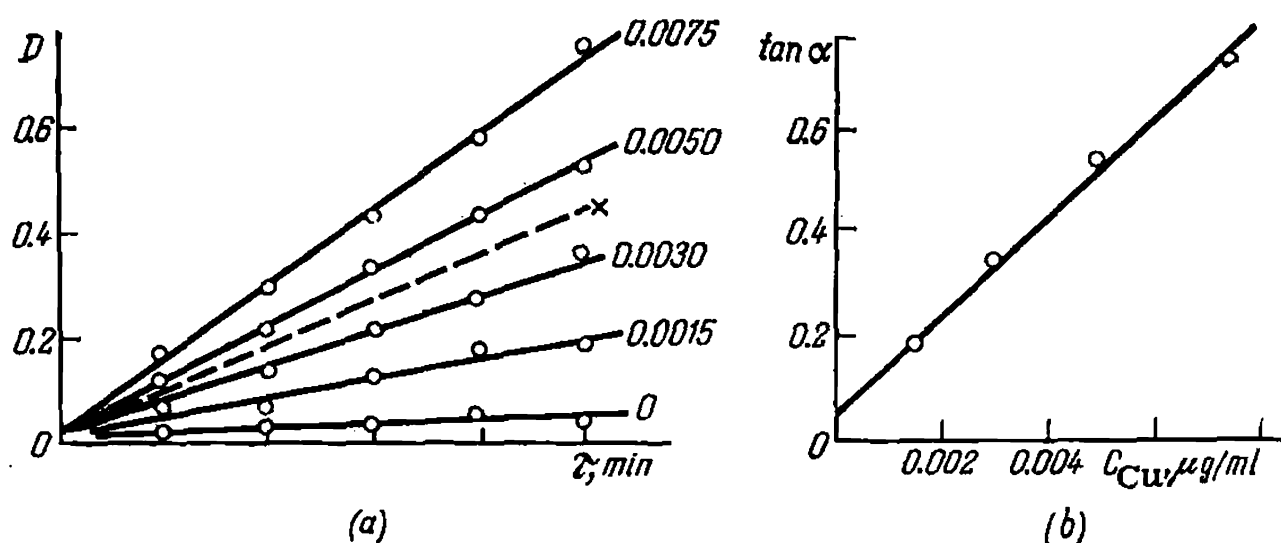


Figure 97

The rate of the reaction is determined from the change in the height of the polarographic wave of Ni 10 minutes after the reaction is started. The data obtained for some initial concentrations of platinum are as follows:

| | | | | | | |
|---------------------------------|-----|------|------|------|------|------|
| $C_{\text{Pt}}, \mu\text{g/ml}$ | 0 | 0.25 | 0.50 | 0.75 | 1.00 | 1.25 |
| h_{Ni}, mm | 100 | 76 | 56.5 | 44.8 | 34.8 | 24.6 |

For the unknown concentration of Pt the wave height of Ni was found to be 41 mm after 10 min under the same conditions.

Find the concentration of platinum.

Solution: For the method of the fixed time of slow reactions we plot a calibration graph of h_{Ni} vs. C_{Pt} , and for fast reactions we construct a plot of $\log h_{\text{Ni}}$ vs. C_{Pt} (see Fig. 98). Having plotted both graphs, we can easily see that no linear relation exists for the first graph. This is evidence that the reaction is sufficiently fast. From the graph shown in Fig. 98 we find that for the wave height 41 mm ($\log 41 = 1.61$) the concentration of the platinum solution is $0.83 \mu\text{g/ml}$.

Example 3. The slow reaction of oxidation of lucigenin by hydrogen peroxide is accompanied by a decrease in the luminescence of lucigenin and is catalyzed by osmium. The

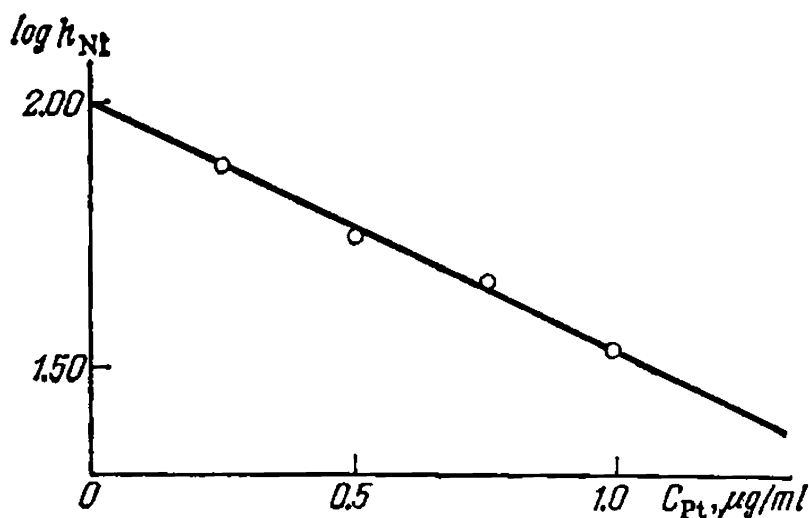


Figure 98

luminescence of standard solutions amounts to 25 units on the scale of a luminescence photometer after the following time intervals:

| | | | | | | |
|--------------------------|------|------|------|-----|------|------|
| $C_{Os}, \mu\text{g/ml}$ | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| τ, min | 11.2 | 6.25 | 3.55 | 2.7 | 2.17 | 1.83 |

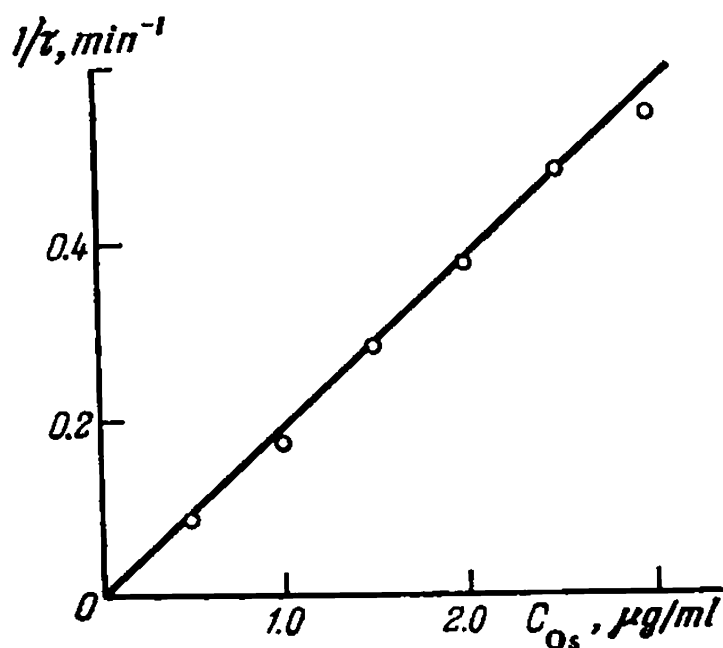


Figure 99

Determine the concentration of osmium in the solution if the value of 25 scale divisions is reached for 4.42 min.

Solution: To solve the problem we make use of the equation for slow reactions:

$$\frac{1}{\tau} = \left(\frac{k}{C_{\text{In}}} \right) C_{\text{cat}}$$

Now we plot a graph of $1/\tau$ versus C_{cat} :

| | | | | | | |
|----------------------------|-------|-------|-------|-------|-------|-------|
| C_{cat} | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
| τ , min | 11.20 | 6.25 | 3.55 | 2.70 | 2.17 | 1.83 |
| $1/\tau$ | 0.090 | 0.160 | 0.285 | 0.370 | 0.475 | 0.545 |

The graph obtained is shown in Fig. 99. Using this graph, we determine the concentration for the unknown sample from the value of $\tau = 4$ min 25 sec or 4.416 min; $1/\tau = 0.226$; $C_{\text{Os}} = 1.20 \mu\text{g/ml}$.

2. PROBLEMS

1. Ruthenium catalyzes the reaction of reduction of Fe^{3+} by tin chloride. For a solution containing different amounts of ruthenium there have been obtained the following values of the optical density of iron rhodanide as a function of time:

| | | | | | |
|-------------------------------------|------|------|------|------|------|
| τ , min | 3 | 4 | 5 | 6 | 7 |
| Without ruthenium | 0.55 | 0.50 | 0.46 | 0.43 | 0.40 |
| 2.4×10^{-6} g Ru | 0.48 | 0.42 | 0.36 | 0.31 | 0.26 |
| 4×10^{-6} g Ru | 0.42 | 0.35 | 0.28 | 0.21 | 0.15 |

Find the content of ruthenium in the solution if under the same conditions the values of the optical density of the solution vary with time as follows:

| | | | |
|------------------------|------|------|------|
| τ , min | 3 | 5 | 7 |
| D | 0.39 | 0.32 | 0.23 |

2. In a kinetic determination of vanadium by the standard addition method the rate of the oxidation of potassium iodide by hydrogen peroxide is controlled by the optical density of a coloured solution of iodine with starch.

Determine the content of vanadium in the solution if the optical density of the solutions varies with time as follows:

| | | | | | |
|--|------|------|------|------|------|
| τ , min | 2.0 | 3.0 | 4.0 | 5.0 | 7.0 |
| Sample containing no vanadium | 0.08 | 0.12 | 0.17 | 0.21 | 0.29 |
| Same sample with 0.3 μg of vanadium added | 0.20 | 0.30 | 0.40 | 0.50 | 0.69 |

3. In the presence of tartaric acid, vanadium catalyzes the reaction of oxidation of the iodide ion by the bromate ion. The course of the reaction is followed by the change of the polarographic wave of BrO_3^- with time. When plotting a calibration graph the following values were obtained for the wave height:

| Concentration of vanadium, $\mu\text{g-ion/ml} \cdot 10^6$ | 0 | 3 | 5 | 7.5 | 10 |
|--|-----|-----|----|-----|-----|
| Wave height, mm, after | | | | | |
| 0 min | 110 | 102 | 95 | 105 | 100 |
| 2 min | 108 | 97 | 89 | 95 | 88 |
| 4 min | 107 | 95 | 84 | 85 | 77 |
| 6 min | 108 | 91 | 79 | 78 | 65 |
| 8 min | 105 | 87 | 71 | 68 | 55 |
| 10 min | 103 | 79 | 65 | 62 | 47 |

The solution under study was diluted 25-fold and after 2.5 ml of this solution was added to a mixture of potassium iodide and bromate the following data were obtained:

| | | | | | |
|------------------------|----|----|----|-----|----|
| τ , min | 0 | 3 | 6 | 8.5 | 10 |
| h , mm | 90 | 81 | 69 | 62 | 58 |

Find the concentration, in $\mu\text{g/ml}$, of vanadium in the solution.

4. The reaction of oxidation of alizarine by hydrogen peroxide is catalyzed by cobalt salts (see Fig. 100). When

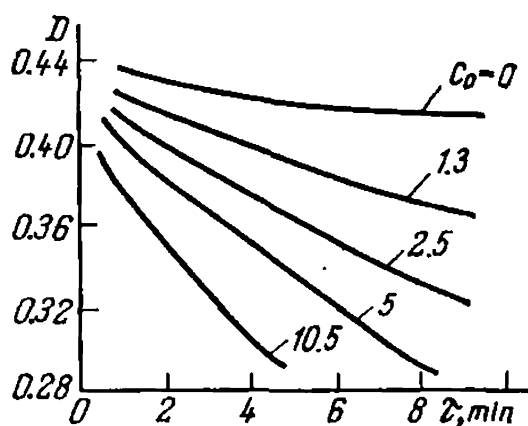


Figure 100. Variation of the optical density of solution with time at various concentrations of cobalt. The numbers on the curves signify the concentration of Co in $(\text{moles/litre}) \times 10^{-5}$.

extracting cobalt diethyldithiocarbamate with 10 ml of chloroform from 100 ml of the aqueous phase the optical density of the chloroform layer was 0.54. After adding 0.25 ml of a solution with a cobalt concentration of 10 mg/ml

the optical density increased to 0.68. To 100 ml of the mixture being catalyzed was added 2 ml of the aqueous phase and the following values of optical density were obtained depending on time:

| | | | | | |
|--------------|-----------|------|------|------|------|
| τ , min | | 2 | 5 | 7 | 10 |
| D | | 0.42 | 0.36 | 0.33 | 0.30 |

Determine the extent to which the cobalt is extracted (in per cent).

5**. Figure 101a shows the curves representing the intensity of chemiluminescence of luminol with copper

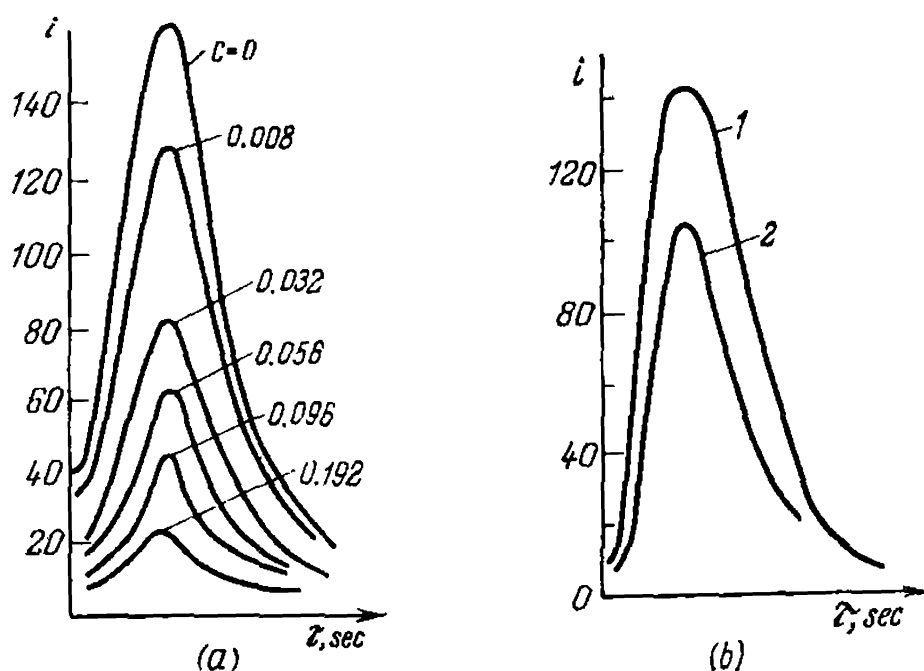


Figure 101

ammoniate and hydrogen peroxide versus time at different contents of phloroglucine, the inhibitor of this reaction (the numbers on the curves indicate the content of phloroglucine in mg/ml).

In analysing the unknown solution of phloroglucine the curves shown in Fig. 101b were obtained before addition (1) and after addition (2) of the solution of luminol with copper ammoniate.

Find the concentration, in moles per litre, of phloroglucine in the solution.

6. Microquantities of molybdenum in a solution are determined by the reaction of oxidation of the iodide ion by hydrogen peroxide, which is accelerated catalytically by

molybdenum. The rate of the reaction is controlled by the value of the optical density of a coloured solution of iodide with starch.

Calculate the content of molybdenum (in $\mu\text{g}/100\text{ ml}$) in the solution being analysed if the variation of the optical densities of the standard and unknown solutions with time is characterized by the following:

| τ , min | 1.5 | 3.0 | 5.0 | 7.0 |
|--|------|------|------|------|
| Optical density of solutions containing molybdenum | | | | |
| 0 $\mu\text{g}/100\text{ ml}$ | 0.03 | 0.05 | 0.10 | 0.13 |
| 0.1 $\mu\text{g}/100\text{ ml}$ | 0.04 | 0.09 | 0.15 | 0.21 |
| 0.2 $\mu\text{g}/100\text{ ml}$ | 0.06 | 0.13 | 0.21 | 0.29 |
| 0.3 $\mu\text{g}/100\text{ ml}$ | 0.08 | 0.16 | 0.26 | 0.37 |
| Optical density of the unknown solution | 0.07 | 0.14 | 0.23 | 0.33 |

7. The concentration of iron is determined by the reaction of oxidation of acidic chromium dark-blue by hydrogen peroxide, the reaction being accelerated catalytically by iron. At iron contents of 0.01, 0.02, and 0.03 $\mu\text{g}/\text{ml}$ the optical densities of the solutions decreased for 8 minutes from 0.40 to 0.30, 0.18, and 0.10, respectively.

Calculate the concentration of iron in the unknown solution, given that the initial optical density of the solution analysed decreased for 8 minutes under the same conditions from 0.40 to 0.25.

8. The reaction of oxidation of ammonia to NO_2^- by hydrogen peroxide is catalyzed by cobalt. The resulting ion NO_2^- is determined by the colour formed with guaiacol (*o*-methoxyphenol) in a sulphuric acid medium. Five minutes after the addition of the reagent the following values of the optical density were obtained for solutions with different amounts of cobalt:

| | | | | | |
|-------------------------------|------|------|------|------|------|
| C , $\mu\text{g}/\text{ml}$ | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
| D | 0.08 | 0.28 | 0.50 | 0.72 | 0.88 |

A 0.8-g sample of an alloy containing traces of cobalt was dissolved in acid and the resulting solution was diluted to 100 ml. The optical density of ammonia solution after adding to it 2 ml of the resulting solution was found to be equal to 0.62 in 5 minutes under the indicated conditions.

Determine the percentage content of cobalt.

9. The reaction of oxidation of the thiosulphate ion is catalyzed by titanium. The course of the reaction is followed by the increase in the turbidity of the solution due to the BaSO_4 suspension formed. In a phototurbidimetric investigation there was noted the time during which permanent turbidity was achieved, corresponding to the optical density 0.25. Depending on the concentration of titanium the following data were obtained:

| | | | | | |
|---|------|-----|-----|-----|-----|
| C_{Ti} , $\mu\text{g/litre}$ | 1 | 3 | 5.5 | 7.0 | 10 |
| τ , sec | 2000 | 750 | 400 | 292 | 214 |

From a sample of a mineral weighing 0.055 g, which was fused and treated, there was obtained 100 ml of a solution. After the addition of 1 ml of the resulting solution to a solution containing a thiosulphate ion, the optical density 0.25 was reached in 345 seconds.

Find the percentage content of TiO_2 in the mineral. The volume of the solution analysed photometrically was 50 ml in all the cases.

10**. The catalytic reaction of oxidation of the iodide ion by hydrogen peroxide is catalyzed by tungsten. The course of the reaction is traced by the increase of the current between the electrodes dipped into 50 ml of the solution. In an analysis by the fixed-concentration method, the time during which a current of 25 mA was reached was noted. Depending on the concentration of tungsten the following data were obtained:

| | | | | | | |
|--|----|------|------|------|------|------|
| C_{W} , mole/l $\cdot 10^2$ | 0 | 2 | 4 | 6 | 8 | 10 |
| τ , min | 25 | 7.43 | 4.55 | 3.22 | 2.38 | 1.95 |

A sample of a single crystal of cadmium sulphide weighing 0.250 g was dissolved and after treatment the solution was diluted to 50 ml. For 1 ml of the resulting solution containing tungsten as an impurity a current of 25 mA was attained in 5 min 28 sec.

Find the concentration of tungsten in the cadmium sulphide (in atoms per cm^3).

11. The oxidation of phenylenediamine by potassium iodate resulting in the formation of coloured products is catalyzed by tungsten ions. In a determination by the fixed-

time method the following values of optical density were obtained in 15 min at different concentrations of tungsten:

| | | | | | |
|------------------------|------|------|------|------|------|
| C , $\mu\text{g/ml}$ | 0 | 0.25 | 0.60 | 0.75 | 1.00 |
| D | 0.12 | 0.38 | 0.60 | 0.74 | 0.93 |

A 1.5-g sample of the slags of tungsten production was dissolved in acid; the resulting solution was treated and diluted to 100 ml. In 15 min the optical density of 5 ml of this solution was 0.67.

Determine the loss of tungsten in 1 ton of the slags. The volume of the coloured solution was 100 ml in all the cases.

12*. Determine the electrical conductance of a 0.1*N* solution of CuCl_2 at 20 °C if the capacity of the cell is 25 ml, the area of the electrodes, 0.75 cm^2 , and the distance between them, 0.5 cm. How will the conductance change during electrolysis in 10 min at a current of 1.5 A?

13**. An alcoholic solution of *l*-menthone and α -secondary butyl bromide in a tube 10 cm long rotates the plane of polarized light $+3.2^\circ$.

Determine the contents of these substances in the solution if the specific rotations of the polarization plane for them are -29.6 and $+10.8^\circ$, respectively, and the mass of the dry residue is 12.56 g.

14. For diallylaminoethylmethacrylate the diffusion current constant in a formamide solution is 3.45 $\mu\text{A/mmole}$, and after the addition of phenol it becomes equal to 4.08 $\mu\text{A/mmole}$. For diallylaminoethylacrylate the corresponding values are 2.16 and 4.34 $\mu\text{A/mmole}$, respectively. The diffusion current of a mixture of these substances in aqueous solution of dimethylformamide was found to be 13.38 μA , and after the addition of an equal amount of phenol it became equal to 10.59 μA .

Find the concentration of the constituents (the dilution of the solution after the addition of phenol is to be taken into account).

15. In the photometric determination of iron by the rhodanide method a 0.1*M* solution of iron rhodanide is diluted 20-fold and at a 100 per cent excess of the reagent the overall error of the determination is ± 10 relative per cent. When the iron content is determined by the spectral method, in

three standards, the error does not exceed ± 5 relative per cent.

Figure out whether the photometric method can yield more accurate analytical results than the spectral method, and if this is possible, under what conditions?

The error in the photometric method is determined only by measurements and by the deviation from the Bouguer-Lambert-Beer law upon dilution of the coloured solution. According to the procedure of photometric analysis the coloured solution should, of necessity, be diluted not less than 20-fold.

16. The distribution ratios in the extraction of vanadium by diisooallylpyrophosphoric acid from 0.5*N* hydrochloric acid are 50 for V^{IV} and 5.5 for V^V , and from 10*N* hydrochloric acid, 2.8 and 83, respectively. At 560 nm the molar extinction coefficient of the extract of V^{IV} is 200 and that of V^V , 670. After extraction from 0.5 and 10*N* hydrochloric acid the optical densities of the extracts in a cuvette with a layer thickness of 2 cm were, respectively, 0.61 and 1.61.

Determine the concentrations of V^{IV} and V^V in the original solution (in moles per litre) if during the extraction the ratio of the volumes of the organic and aqueous phases was 1 : 10.

17. The angle of rotation of the plane of polarized light for a mixture of glucose ($[\alpha] = +55.5^\circ$) and fructose ($[\alpha] = -96^\circ$) in a tube 10 cm long at $\lambda = 546$ nm is -7.95° . A 10-ml volume of a solution of the mixture of the sugars is decomposed by potassium borohydride and the amount of the borohydride that has not reacted is determined after the reaction from the quantity of H_2 evolved upon decomposition of HCl.

Determine the content of glucose and fructose in 100 ml of the solution if it is known that from the potassium borohydride required for 10 ml of the solution to be decomposed there was evolved 240 ml of H_2 before the reaction and 72 ml after the reaction was complete.

18. For the extraction-photometric determination of silver it is extracted with diethyldithiophosphate containing radioactive phosphorus, ^{32}P . The silver complex obtained is extracted with CCl_4 , whose activity is measured. In a blank experiment the activity of CCl_4 was 125 counts per

minute. A standard sample containing 50 μg of silver in 50 ml showed an activity of 3820 counts per minute after the extraction of 10 ml of CCl_4 . From a 1.2-g sample of the material under study there was obtained, after appropriate treatment, 25 ml of a solution, from which a complex of silver with diethyldithiophosphate was extracted with 10 ml of CCl_4 . The activity of the extract was found to be equal to 1220 counts per minute.

Find the percentage content of silver in the mineral.

19. To determine the distribution coefficient in the extraction of Fe^{3+} from a hydrochloric solution with an equal volume of ethyl ether, use was made of the photolorimetric and potentiometric methods. The quantity of Fe^{3+} left in the hydrochloric acid solution was diluted to 100 ml and then determined photolorimetrically; the optical density was found to be equal to 0.300. In the organic phase, iron was determined potentiometrically; after appropriate treatment the volume of the iron solution was equal to 50 ml. The solution of the reduced iron was titrated with a solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in an acidic medium, the titre of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution with respect to iron(II) being 0.00032. The following data were obtained:

| | | | | | | | | |
|--|------|------|------|------|------|------|------|------|
| $V_{\text{K}_2\text{Cr}_2\text{O}_7}$, ml | 5 | 6 | 6.5 | 7.0 | 7.5 | 8.0 | 8.25 | 8.50 |
| E , mV | 435 | 431 | 435 | 438 | 450 | 500 | 545 | 600 |
| $V_{\text{K}_2\text{Cr}_2\text{O}_7}$, ml | 8.75 | 9.00 | 9.25 | 9.50 | 10.0 | 10.5 | 11 | |
| E , mV | 655 | 700 | 728 | 750 | 753 | 756 | 760 | |

To plot a calibration graph in the photometric determination the following values of optical density versus the iron concentration were used:

| | | | | |
|-----------------|------|------|------|------|
| C , mg/100 ml | 0.2 | 0.4 | 0.6 | 0.8 |
| D | 0.21 | 0.40 | 0.59 | 0.78 |

Determine the distribution coefficient for trivalent iron between water and ethyl ether.

20**. A sample of a single crystal of cadmium selenide was dissolved in acid and diluted to 25 ml. A 5-ml aliquot of this solution was treated for a polarographic determination of cadmium and diluted to 10 ml. The polarographic peak corresponded to 3.6 μA . The peak of cadmium at its concentration of 0.1 mg/ml corresponded to 1.9 μA .

Selenium in the cadmium selenide solution was determined photometrically. To this end, a 2-ml aliquot of the solution after appropriate treatment was diluted to 25 ml and the optical density of the solution was found to be equal to 0.35. When 1 ml of a standard solution with a selenium concentration of 0.1 mg/ml was added to this solution, the optical density increased to 0.42.

Find the excess phase in the single crystal (in mol. per cent).

21**. In the analysis of a single crystal of a semiconducting sample, whose composition was expected to be CdGeAs_2 , cadmium and germanium were determined polarographically and arsenic photometrically. The dissolution of a 25-mg sample gave 10 ml of the solution. To determine cadmium polarographically 1 ml of the solution was diluted with a background solution to 10 ml and the peak of cadmium corresponded to 18.9 mA. After the addition of 1 ml of a standard solution with a cadmium concentration of 1 mg/ml the peak was found to correspond to 38.4 mA. To determine germanium, a 2-ml aliquot treated appropriately resulted in 5 ml of the solution; the peak of germanium corresponded to 10.3 mA. When a standard solution with a germanium concentration of 0.2 mg/ml was analysed polarographically, the peak corresponded to 11.7 mA. For the photometric determination of arsenic 1 ml of the original solution was treated appropriately and diluted to 35 ml; the optical density was found to be 0.58. After the addition of 0.0250 mg of arsenic it increased to 0.89.

Find out whether the single crystal corresponds to the given composition. Determine the amount and the composition of the excess phase.

22. Nickel is extracted from a 100-ml volume of aqueous solution in the form of dimethylglyoximine with 10 ml of chloroform and the extract is diluted with chloroform to 25 ml. Aliquots (5 ml) of the solution are analysed photometrically by the standard addition method.

Calculate the content of nickel in the unknown solution (in μg) allowing for the extent of extraction, given that the optical densities of the chloroform extracts with 20 μg of nickel added and without addition of nickel are 0.45 and 0.20, respectively. The distribution coefficient of nickel

dimethylglyoximine in the chloroform-water system is 410.

23. The process of complex formation of zinc ions with pyridyl-2-azoparadimethylaniline is studied by the potentiometric method. The value of the stability constant calculated from experimental data and extrapolated to the zero ionic strength of the solution is 229 at 25 °C and 208 at 35 °C.

Calculate the thermodynamic characteristics of the complex-formation process and write the most probable equation for the reaction if the composition of the complex formed is known to be in the ratio 1 : 1.

Directions for Solving Problems and Answers

1. DIRECTIONS FOR SOLVING PROBLEMS

Chapter I

23 and 24. From the data of the first series of experiments calculate the error of colorimetric analysis. From the data of the second series of experiments calculate the error of the colorimetric analysis and chemical treatment and then the error of the chemical treatment separately. From the data of the third series of experiments calculate the total error of the determination and then separately the error of taking samples for analysis.

28. When solving the problem it is necessary first to determine C_0 graphically and then to derive an equation of the type indicated.

29. The solubility of the gas, S , is related to the temperature T as follows:

$$\log S = A + \frac{B}{T}$$

Chapter II

20. The concentration of the impurity (in atoms per cm^3) is calculated by the equation

$$n = \frac{x d_{\text{base}}}{A_{\text{imp}}} \cdot 6.02 \times 10^{21}$$

where x is the content in per cent by weight of the impurity.

22. See the directions for Problem 20.

Chapter III

22. See the directions for Problem 20 in Chapter II.

30. Calculate the average value of the photometer readings as a function of time and use it to determine the amount of NO_2 .

37, 38. Plot a graph of the optical density against the ratio of the concentrations of cobalt and nitroso-R-salt and determine, from the inflection point on it, this ratio at the moment of complete complex-formation.

39. For data on the infrared spectra of xylenes see Kössler, I., *Methoden der Infrarot-Spektroskopie in der chemischen Analyse*, Akademische Verlagsgesellschaft, Leipzig, 1961.

41. For tabulations of characteristic frequencies see K. Nakanishi, "Infrared Absorption Spectroscopy", Tokyo, 1962.

Chapter IV

17. From the data of the analysis calculate the formula of the compound and its molecular weight. Compute its molar refraction and compare it with possible variants of bonds in this compound and their group refractions.

Chapter V

11. From the value of the concentration determine by the formula the specific rotation of the polarization plane and then calculate the rotation for the given concentration.

14. From the value of the rotation of the polarization plane at an arbitrarily chosen value of specific rotation of the polarization plane determine the concentration of the solution and then recalculate, taking into account the value of the specific rotation at the concentration found.

Chapter VI

13. See the directions to Problem 20 in Chapter II.

18. See the directions to Problem 30 in Chapter III.

Chapter VII

13. Plot the calibration graph representing n as a function of $\log C$, assuming $n \sim I_{\text{rel}}$; the segments corresponding to the one-order change of the concentration on both axes must be equal.

14. For the composition of brass see a handbook of metallurgy; the corresponding spectral lines can be found in tables of spectral lines.

15. Make use of the formula of thermal excitation

$$N_{\text{ex}} = AN_0 e^{-E_{\text{ex}}/kT}$$

where N_{ex} is the concentration of excited atoms; N_0 is the total concentration of neutral atoms in the light source; E_{ex} is the energy of the excited level, eV.

Assume $A = 1$; $k = 8.616 \times 10^{-5}$ eV/deg.

17. See Vainshtein, E. and M. Kakhan, "Reference Tables for X-Ray Spectroscopy", Izd. Akad. Nauk SSSR, 1953 (in Russian).

20. Measure the ratio of the line intensities of niobium and titanium, $I_{\text{Nb}}/I_{\text{Ti}}$, from the characteristic curve of the spectrum for the original sample and for the spectrum of the sample to which niobium has been added. Plot a graph of ΔC_1 versus $I_{\text{Nb}}/I_{\text{Ti}}$ on the basis of these two points with abscissas $\Delta C = 0$ and $\Delta C = 0.2$ per cent.

Continue the graph until it intersects the abscissa axis. The sought-for concentration C_x is equal to the absolute value of the abscissa of the intersection point.

21. Use the formula

$$C_{\text{Mn}}\% = \frac{100 - (a + C_{\text{Si}})}{1 + C_{\text{Fe}}/C_{\text{Mn}}}$$

where a is the sum total of the impurities not determinable by the spectral method.

24. Determine $\log I_{\text{an}}$ in each spectrum of the sample, average out the results and determine C from $\log I_{\text{an}}$.

26. Use the formula which is usually resorted to for calculating analytical errors from the errors of readings

$$\frac{\Delta C}{C} = \frac{2.3\Delta n}{kbn}$$

where k is the number of divisions per one order of concentration; b is the slope of the calibration curve.

That the calibration graph has changed is evidenced by the fact that the trial reading differs from the previous one by more than $2\Delta n/\sqrt{3}$ (Δn is the rms error of the measurement of the quantity n). To check out, plot calibration graphs for $k = 400$ mm (see the directions to Problem 13).

30. See the explanation to Problem 17.

Chapter VIII

20. Set up two equations, one for the mass of the deposit and one for the current consumed to deposit a mixture of the metals.

Chapter XI

26. Set up two equations for the current intensity before and after the addition of phenol.

27. Using the graph of the temperature dependence, reduce the wave height at 45° to that at 30° and determine the concentration from the calibration graph.

29. The diffuse nature of the wave is to be checked by the linearity of the graph in the coordinates $\log i/(i_d - i)$ versus E .

From the data obtained, determine the wave height for the height of the mercury column 360 mm and calculate the concentration from the calibration graph.

30, 31. The methods of calculating the stability constants of complexes are covered in the book by Rossotti, F. and Rossotti, H., "The Determination of Stability Constants and Other Equilibrium Constants in Solution", New York-London, 1961.

Chapter XII

23. Having chosen the values of m/e , for which the percentage is the largest for the given constituent, set up simultaneous equations and solve them to determine the content in the mixture.

25. Draw the peaks on graph paper and calculate their areas.

Chapter XIII

13. Plot a graph representing the relation between the concentrations in the logarithmic system of coordinates and determine the constants of the equation.

Chapter XIV

5. From the data of the figure construct a graph of the relative decrease of the chemiluminescent intensity as a function of the concentration of phloroglucine and use this graph to determine the unknown concentration by calculating for it the relative decrease of the chemiluminescence.

10. See the directions to Problem 20 in Chapter II.

13. On the basis of the mass of the precipitate and the rotation of the polarization plane, set up two equations and find the concentrations by using these equations.

20, 21. Calculate the content of the components in molar fractions and separate out the fraction for cadmium selenide to determine the excess phase.

2. ANSWERS TO PROBLEMS

In solving problems on physicochemical methods of analysis one has often to plot graphs and calibration curves. The ultimate result depends on the scale chosen and the accuracy in plotting the curve. In calculations, use may be made of tables of logarithms, slide rules, and calculating machines; the answer may vary, depending on what is used for calculations. The standardization of plotting graphs and the calculating means employed is outside the scope of this book. Therefore, the 3 to 5 per cent deviation from the values given in the answers should not be thought of as errors. Such a deviation lies within the limits of the ordinary accuracy of physicochemical measurements in laboratory conditions.

Chapter I

2. Multivariant Problems

1. I. 91.2 ± 1.4 . II. 42.43 ± 2 . III. $8.8_{-2.4}^{+2.1}$. IV. 978 ± 3 . V. 19.5 ± 0.6 . VI. 0.049 ± 0.009 . VII. 171_{-20}^{+8} . VIII. $11.4_{-1.5}^{+0.9}$.

2. I. $x - \log(1/y)$. II. $x - (1/\log y)$. III. $\log(1/x) - y$. IV. $1/x - \log y$. V. $1/\log x - \log y$. VI. $\log x - y$. VII. $1/\log x - 1/y$. VIII. $x^3 - y^2$.

3. I. $C = 55.6 \pm 0.2$ per cent. II. $C = 0.055 \pm 0.003$ per cent. III. $C = (3 \pm 1) 10^{-5}$ per cent. IV. $C = 15.2 \pm 0.1$ per cent. V. $C = 115.1 \pm 0.2$ mg. VI. $C = 9.66 \pm 0.03$ per cent. VII. $N = 0.034 \pm 0.0001$. VIII. $C = 2.63 \pm \pm 0.02$ per cent.

3. Problems

1. (31.1 ± 0.1) per cent.

2. *First analyst*: random error ± 0.06 per cent, systematic error $+0.01$ per cent, two measurements—crude errors for the criterion 3σ . *Second analyst*: random error ± 0.02 per cent, systematic error $+0.09$ per cent, four measurements—crude errors for the criterion 3σ .

3. *First analyst*: $\sigma = 6.4$, four crude errors, negative systematic error. *Second analyst*: $\sigma = 7.0$, three crude errors. *Third analyst*: $\sigma = 2.9$, two crude errors.

4. $\sigma = 1.5$ μg . At small concentrations the systematic error is negative and at high concentrations it is positive.

5. 83.88 mA.

6. $V_1 = 12.72$ ml, $V_2 = 18.68$ ml.

7. $M = 87.8 \pm 0.7$. The greatest error is due to temperature measurement.

8. 2.67.

9. $(3.560 \pm 0.006) 10^{-3}$. The largest error is due to the measurement of the volume with a pipette and burette.

10. $A = -14 + 3.7 B$.

11. $(1.15_{-0.09}^{+0.14}) 10^{-3}$.

12. The coordinate system $\frac{1}{\log \frac{P}{A}}$ vs. $1/t$.

13. $C_{\text{Cu}} = 11.48 \pm 0.01$ per cent. The systematic error is -0.10 per cent.

14. $C_{\text{MgCl}_2} = (0.0106 \pm 0.0001)$ g/ml. All the series of determinations for the Q -criterion are comparable.

15. $t_1 = 7.88^\circ\text{C}$, $t_2 = 18.22^\circ\text{C}$.

16. 0.121 ± 0.01 .

17. $\log C = -0.966 \pm 0.675 \log \Delta$.

18. $R = 26.19 \pm 0.03$. The error in all the measurements is approximately the same.

19. $\log \eta = -0.235 + 125/T$, $T = 423^\circ\text{C}$.

20. $C_w^{1.68}/C_b = 5.4 \times 10^{-2}$; $C'_w = 5.25 \times 10^{-2}$, $C''_w = 4.47 \times 10^{-2}$.

21. The systems of coordinates: $\log \log 100 y$ vs $\log \sin x$; 10^y vs. $1/\sin x$; $1/\log y$ vs. $\log x$.

22. The compound is $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$. *First analyst*: $\varepsilon_\alpha = 0.0007$. *Second analyst*: $\varepsilon_\alpha = 0.0004$. *Third analyst*: $\varepsilon_\alpha = 0.0021$.

23. $C_{\text{Ni}} = 2.50 \pm 0.20$ per cent. Sampling, $\varepsilon = 0.03$; sample treatment, $\varepsilon = 0.14$; determination, $\varepsilon = 0.01$.

24. Sampling, $\varepsilon = 0.01$; sample treatment, $\varepsilon = 0.08$; determination, $\varepsilon = 0.06$.

25. $C_{\text{Zn}} = 3.50 \pm 0.06$. The determinations involve many (up to 60%) crude errors.

26. $i = 0.50 + 6 \times 10^{-3} t$; $t = 225^\circ\text{C}$.

27. 100.06 ml.

28. $C_0 = 2.32$ per cent; $C_0 - C_\tau = -0.79 + 1.57 \log \tau$, $\tau = 80$ min.

29. $\log P = -3.525 + 10^3/T$, $t = 308^\circ\text{C}$.

30. $y^3 = 3.48/x^2$.

31. $\Delta\lambda = 2(\Delta r + \Delta a + \Delta b)$.

4. Assignments for Programmed Questioning

1. (d). 2. (b). 3. (d), (f), (h). 4. (b), (c), (h). 5. (c), (e), (f). 6. (a)—5; (b)—4; (c)—6; (d)—2; (e)—1; (f)—3. 7. (a)—4; (b)—7; (c)—7, 1; (d)—8; (e)—7, 3; (f)—5; (g)—2; (h)—6. 8. (a)—6, 2; (b)—4, 2; (c)—1, 5; (d)—2, 2; (e)—3, 2; (f)—7, 1; (g)—5, 7. (The first figure refers to group B and the second to group C.) 9. (a)—1, 5; (b)—2, 3; (c)—2, 3; (d)—6, 7; (e)—3, 5; (f)—10, 5; (g)—11, 7; (h)—8, 3. (The first numbers refer to graphs in Fig. 4 and the second to group B.) 10. A—(c); (a)—4; (b)—1; (d)—3; (e)—2.

Chapter II

2. Multivariant Problems

1. I. 0.016. II. 0.128. III. 8×10^{-4} . IV. 0.120. V. 0.28. VI. 0.465. VII. 0.75. VIII. 0.22.
2. I. 10.75. II. 0.195. III. 112. IV. 136. V. 10.7. VI. 0.54. VII. 0.33. VIII. 84.7.
3. I. 4.4. II. 1.46. III. 405. IV. 5.15. V. 18.1. VI. 27.8. VII. 8.25×10^{-4} . VIII. 40.

3. Problems

1. 35 per cent of the initial. 2. 0.37 per cent. 3. 33.3 per cent. 4. 0.025 per cent. 5. 14.05 per cent. 6. 2950 mg/litre. 7. 22.5 mg/litre. 8. 1.12 per cent. 9. 1.29 per cent. 10. 0.29 per cent. 11. 8.40 per cent. 12. 176 mg/litre. 13. 2.2 cm. 14. 18.6 per cent. 15. 0.321M. 16. 39.2 kg of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. 17. 4.99 per cent. 18. 3.9 mg/litre, the error without corrections made is 7 per cent. 19. $C = 2.4 \pm 0.1$, the largest error is due to the weighing made to prepare standards. 20. 1.17×10^{18} atoms per cm^3 . 21. The concentration can be measured from 0.24 to 490 mg/ml. 22. The weight of the sample is 26.6 mg. 23. 2.22×10^{-2} per cent. 24. 0.445 per cent. 25. $C = 4.65 \text{ mg/m}^3$, which exceeds the permissible value by a factor of 15.5. 26. 6.06×10^{-2} per cent. 27. 0.64 per cent. 28. $C = (0.67 \pm 0.03)$ per cent P, the main error of the measurement is due to the determination of P in the standard and to the measurement of the layer thicknesses. 29. $C = 562 \text{ mg/ml}$, which exceeds the permissible value by a factor of 11.

4. Assignments for Programmed Questioning

1. (c). 2. (b). 3. (e). 4. (a). 5. (e). 6. (d). 7. (b), (c), (g). 8. (c), (f), (g). 9. (a in Fig. 6)—4; (b)—2; (c)—5; (d)—3; (e)—1; (f)—1; (g)—5; (h)—4. 10. (a)—7; (b)—12; (c)—1; (d)—4; (e)—12; (f)—5; (g)—12; (h)—12; (i)—10.

Chapter III

2. Multivariant Problems

1. I. 0.58. II. 1.1. III. 14.85. IV. 5.12×10^{-3} . V. 5.66. VI. 0.366. VII. 3.16. VIII. 1.48.

2. I. 6.25×10^{-2} . II. 6.74×10^{-2} . III. 6.25. IV. 32.5. V. 5.98. VI. 15.73. VII. 840. VIII. 62.4.

3. I. 2.13. II. 2.27×10^{-4} . III. 1.32. IV. 1.07×10^4 . V. 0.5. VI. 0.121. VII. 0.208. VIII. 1.18×10^{-2} .

3. Problems

1. 0.335. 2. 0.0275 per cent. 3. 5.84 mg/litre. 4. 2.04 per cent. 5. 1.46 per cent. 6. 4650. 7. (6.6 ± 0.8) per cent. 8. 0.44 per cent. 9. 1.29 per cent. 10. 0.118 per cent. 11. 0.186 mg/ml. 12. 0.006 g·eq/litre. 13. 0.3 per cent. 14. (2.87 ± 0.08) per cent. 15. 12.3 g/m³. 16. 7.6×10^{-2} per cent. 17. $C_{\text{Ni}} = 0.10$ per cent, $C_{\text{Co}} = 0.85$ per cent. 18. 0.23 per cent. 19. 6.0 mg. 20. $g/V \simeq 1$. 21. 0.207 mg. 22. 1.17×10^{20} atoms per cm³. 23. 14 per cent. 24. 0.42 µg/ml. 25. 0.236 mg. 26. 1.96×10^{-5} mg/ml. 27. 1.04×10^5 . 28. A = 94.6 per cent, B = 99.0 per cent. 29. $\text{K}_2\text{Cr}_2\text{O}_7 = 3.02$ grams; $\text{CuSO}_4 = 1.21$ grams; the error with no corrections made for $\text{K}_2\text{Cr}_2\text{O}_7$ is 2 per cent, and for CuSO_4 , 53 per cent. 30. 121 kg. 31. Bi = 4.33×10^{-3} gram, Pb = 7.86×10^{-3} gram. 32. $C_{\text{Mn}} = [(2.6D_{425} - 0.147D_{360})/2] \times 10^{-4}$ mole/litre; $C_{\text{Co}} = [(1.23D_{360} - 0.825D_{425})/(3.20 - 0.120)] \times 10^{-4}$ mole/litre. 33. $C = 0.03$ mg/m³, the permissible limit is 0.3 mg/m³. 34. $C_{\text{Cu}} = 3.01 \times 10^{-5}M$, $C_{\text{Co}} = 1.97 \times 10^{-5}M$, $C_{\text{Ni}} = 1.02 \times 10^{-3}M$. 35. $1.61 \times 10^{-8}M$. 36. 7.06×10^{-7} . 37. R: Co = 3 : 1. 38. PAR : Pb = 1 : 1. 39. Ortho-xylene is determined, $C = 1.9 \times 10^{-5}$ g/ml, $D = 1.86 \times 10^4 C$. 40. The concentration of 2,3-dimethylhexane is 0.302M, of 2,5-DMH = 0.528M, of 2,3,4-trimethylpentane, 0.206M. 41. The oscillations with wave numbers 686 cm⁻¹, 750 cm⁻¹, and 3100 cm⁻¹ correspond to the group $\equiv\text{C}-\text{H}$; 2260 cm⁻¹ to $-\text{N}=\text{C}=\text{O}$; 1510 and 1600 cm⁻¹ to $-\text{C}_6\text{H}_5$. 42. $K = 6.37 \times 10^{-12}$.

4. Assignments for Programmed Questioning

1. (b). 2. (d). 3. (c). 4. (a), (e), (f). 5. (b), (d), (g).
 6. (a)—3; (b)—7; (c)—4; (d)—9; (e)—2; (f)—1. 7. (a)—9, 4;
 (b)—5, 6; (c)—11, 6; (d)—1, 8; (e)—3, 5; (f)—6, 3. (The
 first figure refers to group B and the second to group C.)
 8. A—c; (a)—4; (b)—1; (d)—5; (e)—2. 9. (a)—3, 2; (b)—
 2, 5; (c)—4; (d)—5, 1; (e)—1, 2. (The first figure refers to
 group B and the second to graphs in Fig. 18.) 10. Fig. 19
 (c); (a)—3; (b)—4; (c)—5; (d)—3; (e)—3.

Chapter IV

2. Multivariant Problems

1. I. 25.20. II. 19.05. III. 31.92. IV. 12.93. V. 23.81.
 VI. 26.94. VII. 17.42. VIII. 32.36.

2. I. 1.3449. II. 50°04'. III. 1.8053. IV. 62°39'. V. 1.6532.
 VI. 1.5721. VII. 1.3369. VIII. 60°76'.

3. I. 4.49. II. 0.033. III. 22.44. IV. 0.760. V. 0.35.
 VI. 0.153. VII. 4.1. VIII. 20.8 per cent.

3. Problems

1. $C_1 = 15.5$ per cent. 2. $C_1 = 51$ per cent, $C_2 = 93$ per
 cent. 3. $C_1 = 9.6$ per cent, $C_2 = 23.2$ per cent. 4. $6.9 \times$
 $\times 10^{-3}$ g/ml. 5. 1.415. 6. 53.5. 7. 12.9 per cent. 8. 3.97 g/m³.
 9. 16.2. 10. 1.744. 11. 1.246N. 12. 12.3 per cent by volume.
 13. $R = 43.6$; the most suitable structure is $\text{H}_3\text{C}-\text{CH}_2-$
 $-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$. 14. 14.5. 15. 0.32 per
 cent. 17. The structure is $\text{CH}_3-\text{O}-\overset{\text{H}}{\underset{|}{\text{C}}}=\overset{\text{H}}{\underset{|}{\text{C}}}=\overset{\text{H}}{\underset{|}{\text{C}}}-\text{O}-\text{CH}_3$. 18.
 7.21 litres.

4. Assignments for Programmed Questioning

1. (c). 2. Fig. 22 (d). 3. (b). 4. (e). 5. (a), (c), (f), (h).
 6. (a), (d), (h) in Fig. 23. 7. (c), (g). 8. (a), (e), (g).
 9. (a)—5; (b)—9; (c)—1; (d)—8; (e)—2; (f)—10; (g)—3;
 (h)—6; (i)—4. 10. (a)—5; (b)—2; (c)—4; (d)—2; (e)—5;
 (f)—2; (g)—1; (h)—5; (i)—5; (j)—5.

Chapter V

2. Multivariant Problems

1. I. 0.882. II. 0.28. III. -104° . IV. 1.57° . V. 1.32. VI. 172° . VII. 10. VIII. 184.5.

3. Problems

1. 131.2° . 2. 14.60° . 3. 0.048° . 4. $\alpha_{589} = 52^\circ 1'$, $\alpha_{486} = 80^\circ$, $\alpha_{434} = 104^\circ$. 5. 0.60 g/100 ml. 6. 0.67 g/100 ml. 7. $C_1 = 18.0$ per cent, $C_2 = 27.2$ per cent. 8. 0.716M. 9. $66.5 \pm 0.8^\circ$. 10. 1.52 g/100 ml. 11. $\beta_1 = 3.85^\circ$, $\beta_2 = 3.97^\circ$, $\beta_3 = 3.83^\circ$. 12. 59.5 per cent. 13. (3.39 ± 0.08) per cent. 14. 37.1 per cent. 15. 90 per cent. 16. $C_s = 0.51$, $C_{er} = 11.5$ per cent. 17. $C_{pe} = 1.64 \beta_{546}/l$, $C_e = (\beta_{334} - 3.18 \beta_{546})/0.05 l$. 18. 16 per cent saccharose hydrolysed. 19. $C_s = 43.6$ mg/ml, $C_g = 12.5$ mg/ml.

4. Assignments for Programmed Questioning

1. (d). 2. (a). 3. (e). 4. (b). 5. (c). 6. (a), (f), (g). 7. (b), (c), (f). 8. (a), (d). 9. (c), (f), (g). 10. (a)—1; (b)—3; (c)—3; (d)—1; (e)—1; (f)—2; (g)—4; (h)—1; (i)—3; (j)—1; (k)—1.

Chapter VI

1. Problems

1. (35.3 ± 0.7) mg/ml. 2. 0.546 per cent. 3. 10.8 g/m^3 . 4. 53.1 per cent. 5. 1.45×10^{-2} per cent. 6. $11.0 \mu\text{g/ml}$. 7. 1.3×10^{-2} per cent. 8. 1.25 per cent. 9. 1.26×10^{-2} mg/ml. 10. 8.7×10^{-4} g/ml. 11. 0.013 per cent. 12. 7.4×10^{-5} per cent. 13. 5.65×10^{16} atoms per cm^3 . 14. 30 g/m^3 . 15. 0.17 mg/ton. 16. $\left(\frac{1}{I^2} - \frac{1}{I_0^2}\right) = 2.6 \times 10^2 \text{C}$, $C = 2.92 \times 10^{-7}$ g-ion/litre. 17. 7.8 mg/litre. 18. 129.2 kg

2. Assignments for Programmed Questioning

1. (b). 2. (e). 3. (d). 4. (c). 5. (a), (c), (f). 6. (b), (d), (h). 7. Fig. 30: (a)—1; (b)—7; (c)—9; (d)—12. 8. (a in

Fig. 32)—5; (b)—2; (c)—4; (d)—3; (e)—1. 9. (1)—i; (2)—e; (3)—b; (4)—i; (5)—d; (6)—a; (7)—c. (The numbers refer to Fig. 33.) 10. (b), (c), (f).

Chapter VII

2. Multivariant Problems

1 and 2. See tables of spectral lines.

4. I. 0.46. II. 1.5. III. 0.06. IV. 0.89. V. 0.54. VI. 0.07. VII. 0.84.

5. I. 18.98. II. 21.15. III. 345.86. IV. 7.54. V. 641.102. VI. 5.51. VII. 402.344.

6. I. 0.0165; 0.0165. II. 0.0165; 0.033. III. 0.2; 0.2. IV. 0.039; 0.019. V. 0.26; 0.20. VI. 0.125; 0.09. VII. 0.078; 0.078. VIII. 0.13; 0.13.

7. I. 0.32. II. 0.28. III. 0.26. IV. 0.56. V. 0.53. VI. 0.41. VII. 0.50. VIII. 0.38.

3. Problems

1. The linear dispersion will increase by a factor of 2.25. 2. 200 to 320 nm. 3. 66 spectrograms. 4. By 60 mm. 5. The time of illumination should be increased 10 times at a coefficient of $p = 1$. 6. Either the area is to be decreased by a factor of 10 or the voltage, to 800 V. 7. First sample: Cr, 0.1; Ni, under 0.6. Second sample: Cr, 0.45-0.75; Ni, 8-15. Third sample: Cr, 14-18; Ni, 55-61. Fourth sample: Cr, 16-20; Ni, 8-15. 8. First sample: $C_{Mn} = 1.52 \pm 0.16$ per cent, $C_{Si} = 5 \pm 0.015$ per cent, $C_{Mo} = 0.25 \pm 0.02$ per cent, $C_{Cr} = 0.25 \pm 0.025$ per cent, $C_{Ni} = 0.38 \pm 0.04$ per cent. 9. During the interval 0 to 3 hr, $C = 0.086$ mg/litre; 3 to 6 hr, $C = 0.064$ mg/litre; 6 to 9 hr, $C = 0.138$ mg/litre. 10. First sample: $C_{Mn} = 1.18 \pm 0.07$ per cent, $C_{Cr} = 1.24 \pm 0.07$ per cent. 11. In neon, $C = 0.0024 \pm 0.0003$ per cent. 12. First sample: $C = 17.7$ mg/litre ± 25 . 13. $C_{Mn} = 0.050$ per cent, $C_{Mg} = 0.39$ per cent; $C_{Ca} = 2.98$ per cent. 16. $R_{eff} = 0.012$. 17. Will affect the graph plotted along the lines of $CuK\alpha_{1,2}$ and $NiK\alpha_{1,2}$. 19. 0.35 per cent. 20. 0.13 per cent. 21. 80.5 per cent. 22. First sample: $C_{Fe} = 9.1 \pm 0.73$ per cent; $C_{Zn} = 5.9 \pm$

± 0.44 per cent. 23. First solution: $C = 7.25 \pm 0.58$ $\mu\text{g/ml}$. 24. 2.7×10^{-4} per cent. 25. $(5.17 \pm 0.54) 10^{-3}$ per cent. 26. Beginning with the 11th measurement. 27. First standard: $C = (0.99 \pm 0.04) 10^{-2}$ per cent. 28. $C_{\text{Pb}} = 1.69$ per cent $\pm 2\sigma$ $C_{\text{Fe}} = 0.43$ per cent $\pm 2\sigma$. 29. ± 0.4 per cent. 30. Tin brass. 31. The unknown line of lead $L\beta_2$ (in the second order) is 980.24X.

4. Assignments for Programmed Questioning

1. (d). 2. (c). 3. (1). 4. (b). 5. (a), (d), (e). 6. (c), (g). 7. (b), (e). 8. (a)—4; (b)—10; (c)—5; (d)—7; (e)—1; (f)—2; (g)—6; (h)—10. 9. (a)—4, 5; (b)—1, 3; (c)—5, 1; (d)—2, 4; (e)—3, 2. 10. A—(c); B—2.

Chapter VIII

2. Multivariant Problems

1. I. 0.3283. II. 1.572. III. 46.42. IV. 3.24. V. 2.39. VI. 45. VII. 0.343. VIII. 2.116.
2. I. 0.0872 g. II. 88.2 mg. III. 0.0499 g. IV. 80.77 mg. V. 1.5 g. VI. 1.02 g. VII. 0.223N. VIII. 0.014N.
3. I. 1.22. II. 0.93. III. 34.8. IV. 133.3. V. 69. VI. 32.5. VII. 40.2. VIII. 76.

3. Problems

1. $\tau = 2$ min 16 sec, $V = 60$ ml. 3. $g = 83.08$ mg, the metal is gadolinium. 4. $C_{\text{Cu}} = 10.3$ per cent, $C_{\text{Pb}} = 33.5$ per cent. 5. $\tau = 18$ min 30 sec. 6. $C_{\text{ZnO}} = 26.59$ per cent. 7. $\tau = 11$ hr 15 min, $g = 596$ g. 8. 1.89×10^{-4} g. 9. 1.51×10^{-4} g/ml. 10. 4.5 A. 11. $n = 0.332$ g/(A·hr), the metal is aluminium. 12. 0.78 per cent. 13. 306 ml. 14. The residual concentration is $5 \times 10^{-5}M$. 15. $(3.65 \pm 0.08) \times 10^{-3}$ g-eq/litre. 16. 23 min 24 sec. 17. 2.67×10^{-2} g-eq/litre. 18. 4 electrons. 19. 2.94 per cent. 20. $g_{\text{Cd}} = 0.362$ g, $g_{\text{Zn}} = 0.043$ g. 21. 2.64×10^{-2} per cent.

4. Assignments for Programmed Questioning

1. (2). 2. (d). 3. (a). 4. (c). 5. (b). 6. (e). 7. (c), (e), (h). 8. (a), (d), (f), (g). 9. (1)—d; (2)—b; (3)—g; (4)—e; (5)—i. (The numbers refer to Fig. 50.) 10. Fig. 51—3; (b).

Chapter IX

2. Multivariant Problems

2. I. 5.30. II. 1.55×10^{-2} , 318. III. 0.0532. IV. 413. V. 0.048. VI. 1.8. VII. 1.59. VIII. 1.61.

3. I. 1.4×10^{-8} . II. 1.2×10^{-10} . III. 4.7×10^{-8} . IV. 4.2×10^{-9} . V. 7.4×10^{-11} . VI. 8.5×10^{-3} . VII. 6.5×10^{-8} . VIII. 9.6×10^{-6} .

3. Problems

1. $0.0106 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$; $106 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g-eq}^{-1}$. 2. $1.59 \times 10^{-2} \text{ A}$. 3. 231.3 ohms. 4. 0.059 g-eq/litre. 5. 0.504 g-eq/litre. 6. 0.13 g-eq/litre. 7. $C_{\text{HCl}} = 1.13 \text{ g/litre}$, $C_{\text{CH}_3\text{COOH}} = 2.22 \text{ g/litre}$. 8. $0.36 \pm 0.02 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$; $138 \pm 8 \text{ cm}^{-1} \cdot \text{cm}^2 \cdot \text{g-eq}^{-1}$. 9. $63.9 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g-eq}^{-1}$. 10. 1.7×10^{-5} . 11. 1.17×10^{-5} . 12. $\log \chi \times 10^4 = 1.94 + 0.705 \log C$, $C_x = 0.39M$. 13. $2860 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$; 2.35 g-eq/litre. 14. $V_{\text{KOH}} = 6 \text{ ml}$, $V_{\text{NH}_4\text{OH}} = 8.4 \text{ ml}$. 15. 1.88×10^{-5} . 16. $102.1 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{g-eq}^{-1}$. 17. 5.1×10^{-8} , the measuring error does not affect the determination of K . 18. $S = 1.5 \times 10^{-5}M$. 19. $(0.0735 \pm 0.0007)N$. 20. The ratio at the equivalence point is 1 : 2, and the reaction is $2\text{KBrF}_4 + (\text{BrF}_2)_2\text{SnF}_6 \rightarrow \text{K}_2\text{SnF}_6 + 4\text{BrF}_3$. 21. The ratio of sea water to river water is 1 : 2.4; $\chi = 1.0 \times 10^{-2} \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. 22. The ratios at the equivalence points are 1 : 1 and 1 : 2. 23. 475 kg. 24. There is an impurity. 25. 0.484 per cent by volume.

4. Assignments for Programmed Questioning

1. (b). 2. (c). 3. (e). 4. (a). 5. (d). 6. (c). 7. (a), (c), (g), (h). 8. (a)—5; (b)—3; (c)—8; (d)—1; (e)—6. 9. (1)—e; (2)—j; (3)—d; (4)—c; (5)—a; (6)—j; (7)—i; (8)—j. (The numbers refer to Fig. 55.) 10. (a)—4; (b)—7; (c)—2; (d)—5; (e)—i; (f)—3; (g)—8; (h)—5.

Chapter X

2. Multivariant Problems

1. I. +0.308. II. -0.4462. III. -0.4795. IV. -1.900. V. +0.334. VI. -0.435. VII. -0.772. VIII. -0.504.

2. I. 4.78. II. 4.44. III. 4.62. IV. 9.15. V. 3.95. VI. 4.74. VII. 4.01. VIII. 2.95.

3. I. -0.09 . II. -0.297 . III. -0.405 . IV. -0.2608 . V. 1.330. VI. 1.475. VII. 0.447. VIII. 1.21.

3. Problems

1. -0.433 V. 2. -1.674 V, $E_2 = 1.9145$ V. 3. 0.0367 V. 4. 3.3. 5. 0.2207 V. 6. 0.5026 V. 7. 1.12×10^{-2} mole/litre. 8. 0.0495 V. 9. $E_1 = 0.1904$ V, $E_2 = 0.1107$ V. 10. $E_1 = 0.37$ V, $\Delta E_1 = 0.53$; $E_2 = 0.572$, $\Delta E_2 = 0.99$. 13. $E_1 = 1.387$ V, $E_2 = 1.250$ V (No), $E_3 = 0.383$ V, $E_4 = 0.583$ V (Yes). 14. 6.05, 5.70, 9.97, and 14.97 ml. 15. 225 $\mu\text{g/litre}$. 16. 0.046 V. 17. 1.1521 V. 18. 2.03. 19. 0.40 cm^3 . 20. 47.5 ml. 21. $5.26 \times 10^{-5}N$. 22. $1.08 \times 10^{-2}N$. 23. $C_{\text{Ag}} = 2.63 \times 10^{-7}$ g-ion/litre, $V_{\text{Cl}} = 0.68$ cm^3 . 26. 7.70 per cent. 27. 2×10^{-15} . 28. 4×10^{-10} . 29. $E_1 = 1.420$ V, $E_2 = 1.510$ V, $E_3 = 0.98$ V. 30. 0.057 V. 31. $V_{\text{eq}} = 6.12$ ml, $C = 3.9$ mg/litre. 32. $C_{\text{NaOH}} = 1.94 \times 10^{-3}$ g-eq/litre, $C_{\text{Na}_2\text{CO}_3} = 4.5 \times 10^{-15}$ g-eq/litre. 33. 0.0004N. 34. 2.0 per cent. 35. 13.8. 36. 217 mV. 37. $K = 1.8 \times 10^{-5}$, $\alpha = 1.3$ per cent.

4. Programmed Questioning

1. (c). 2. (e). 3. (b). 4. (a), (d), (g). 5. (a), (c), (d), (h). 6. (a)—10; (b)—5; (c)—8; (d)—1; (e)—2; (f)—6; (g)—4; (h)—7; 7. (a)—5 in Fig. 58; (b)—6; (c)—4; (d)—2; (e)—8; (f)—1; (g)—1; (h)—3. 8. (a)—5; (b)—2; (c)—8; (d)—1; (e)—7; (f)—4; (g)—6; (h)—3. 9. Fig. 59—(4); (a). 10. A—(c); B—2.

Chapter XI

2. Multivariant Problems

1. I. 6.00. II. 74.7. III. 5.57. IV. 5.75. V. 0.978. VI. 285.3. VII. 2.53. VIII. 0.656.

2. I. 0.236. II. 0.121. III. 0.119. IV. 0.166. V. 0.073. VI. 0.045. VII. 0.016. VIII. 0.0146.

3. I. 0.0247. II. 0.0021. III. 0.032. IV. 0.0056. V. 1.7×10^{-4} . VI. 0.015. VII. 6×10^{-4} . VIII. 8×10^{-4} .

4. I. 3800; 3250. II. 1520; 5530. III. 380; 6670. IV. 152; 6898. V. 76; 6974. VI. 15.2; 7034.8. VII. 7.6; 7042.4. VIII. 3.8; 7046.2.

5. I. $1/5$. II. $1/750$. III. $1/1$. IV. $1/100$. V. $1/25$. VI. $1/1000$. VII. $1/5000$. VIII. $1/25$.

3. Problems

1. 2.03. 2. $0.0015M$. 3. $12.5 \mu A$. 4. 0.20 per cent. 5. 32.6 mg/litre. 6. $5.6 \times 10^{-5}M$. 7. 7×10^{-2} per cent. 8. $C_1 = 0.0224$ g, $C_2 = 0.0121$ g, $C_3 = 0.0290$ g. 9. 3.75×10^{-4} per cent. 12. Without impurities, $E = -1.80$ V; in the presence of Zn, $E = -0.35$ V or -1.0 V. 13. 2.5×10^{-4} per cent. 14. 2.5×10^{-5} per cent. 15. $E_{1/2} = -0.585$ V, $n = 2$. 16. $K = 1.92$. 17. $D = 3.6 \times 10^{-5} \text{ cm}^2 \cdot \text{sec}^{-1}$, $i = 55.9 \mu A$. 18. 0.078 per cent. 19. 0.022 per cent. 20. $C_{Sb} = 23.4$ per cent, $C_{Sn} = 0.12$ per cent, $C_{In} = 18.7$ per cent, $C_{Cd} = 3.25$ per cent. 21. The temperature coefficient is 2 mm/deg, $C = 4.7$ mmoles/litre. 22. 1.14 mmoles/litre. 23. 0.0083 per cent. 24. The composition of the compound is $CdIn_8SnSb_{10}$. 25. $C = 0.42$ mmole/litre, $n = 2$. 26. $C_{DAMA} = 0.973$ mmole/litre; $C_{DAA} = 3.26$ mmoles/litre. 27. $C = 0.145$ mmole/litre. 28. $D = (2.1 \pm 0.2) 10^{-6}$. 29. 0.16 mg/ml. 30. $K = -7.9 \times 10^{-7}$, the coordination number is 4. 31. $K_{[CuPyr_2]} = 3.55 \times 10^{-6}$, $K_{[CuPyr_3]} = 3 \times 10^{-7}$, the coordination number 4.

4. Assignments for Programmed Questioning

1. (b). 2. (d) in Fig. 66. 3. (d). 4. (a), (c), (f). 5. (b), (d), (h). 6. (a)—7 and 6, 8; (b)—3 and 2; (c)—1, 5 and 5; (d)—8 and 3; (e)—2 and 1. 7. (a)—4, 3; (b)—3, 1; (c)—1, 4; (d)—6, 2; (e)—2, 5; (f)—5, 5; (g)—10, 5. 8. (a)—2, 3; (b)—5, 6; (c)—9, 5; (d)—1, 2; (e)—7, 2; (f)—4, 8; (g)—10, 6. 9. A—(a), (d), (f); B—2, 5; 7. 10. A—(b); B—3.

Chapter XII

2. Problems

1. $C_{CaC_2O_4} = 36$ per cent, $C_{MgC_2O_4} = 41$ per cent; $C_{H_2O} = 20$ per cent, $C_{SiO_2} = 3$ per cent. 2. $C_{CaSO_4 \cdot 2H_2O} = 24.85$ per cent, $C_{CaCO_3 \cdot MgCO_3} = 11.50$ per cent,

$C_{\text{CaCO}_3} = 37.15$ per cent. 3. $C_{\text{H}} = 0.89$ per cent, $C_{\text{O}} = 51.58$ per cent, $C_{\text{Mg}} = 2.18$ per cent, $C_{\text{C}} = 9.49$ per cent, $C_{\text{Fe}} = 7.60$ per cent, $C_{\text{Ca}} = 22.55$ per cent, $C_{\text{Si}} = 5.68$ per cent. 4. Hygroscopic water, 5 per cent; water of crystallization, 40.95 per cent; chemically bound water, 3.41 per cent; the formula of the compound is $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. 5. $C_{\text{Ca}(\text{ClO}_4)_2} = 17.4$ per cent, $C_{\text{CaOCl}_2} = 12.9$ per cent, $C_{\text{Ca}(\text{OH})_2} = 20.0$ per cent, $C_{\text{CaCO}_3} = 7.9$ per cent, $C_{\text{SiO}_2} = 29.8$ per cent, $C_{\text{H}_2\text{O}} = 12$ per cent. 6. 11 per cent. 7. 8— $\text{CH}_4/2$, 13— CH , 14— CH_2 , 15— CH_3 , 16— CH_4 , 28— CO , 44— CO_2 . 8. 59 ± 2 . 10. 1.96 per cent. 11. 2.38×10^{-3} per cent. 12. $C_{\text{CaCO}_3} = 14.1$ per cent, $C_{\text{CaSO}_4} = 4.1$ per cent. 13. 1.26×10^{-5} per cent. 14. 0.108 per cent. 15. 40 mg. 17. 75 to 80 °C—removal of hygroscopic water; 130 °C—removal of three water molecules; 440 to 460 °C—decomposition of $\text{CaCr}_2\text{O}_7 \rightarrow \text{CaO} + 2\text{CrO}_3$; 1070 °C—partial decomposition: $2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + 3\text{O}$. 18. $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O} \rightarrow \text{La}_2(\text{CO}_3)_3 + 8\text{H}_2\text{O}$, $\text{La}_2(\text{CO}_3)_3 \rightarrow \text{La}_2\text{O}_3 \cdot \text{CO}_2 + 2\text{CO}_2$, $\text{La}_2\text{O}_3 \cdot \text{CO}_2 \rightarrow \text{La}_2\text{O}_3 + \text{CO}_2$. 19. $C_{\text{CaCO}_3} = (2.5 \pm 0.7)$ per cent. 20. 14— CH_2 , 28— CO , 42— $\text{CH}_3\text{COOC}_5\text{H}_7$, 44— CO_2 , 57.5— $\text{C}_5\text{H}_{11}\text{COO}$, 59— CH_3COO , 70— C_5H_{10} , 71— C_5H_{11} . 21. 39— C_6H_5 , 50— $\text{C}_6\text{H}_2-\text{C}=\text{CH}_2$, 51— $\text{C}_6\text{H}_3-\text{CH}-\text{CH}_2$, 77— C_6H_3 , 78— C_6H_6 , 103— $\text{C}_6\text{H}_5-\text{CH}-\text{C}$, 104— $\text{C}_6\text{H}_5-\text{CH}-\text{CH}$. 24. $C_{\text{O}} = 5 \times 10^{-5}$ per cent, $C_{\text{Fe}^{+}} = 3.5 \times 10^{-4}$ per cent, $C_{\text{Cd}^{+}} = 2 \times 10^{-4}$ per cent. 25. From the areas, $C = 6.1 \times 10^{-6}$ per cent; from the height, $C = 4.8 \times 10^{-6}$ per cent. 26. 44.5 per cent. 27. 0.11 per cent. 28. 9.95×10^{-10} . 29. 10 mg. 30. 12.2 mg. 31. 0.166M. 32. $C_{\text{Hg}} = 3.6$ mg, $C_{\text{Zn}} = 1.21$ mg. 33. 2.1×10^{-7} . 34. $S = 3.98 \times 10^{-3}$, $SP = 1.6 \times 10^{-5}$. 35. After the first distillation, $C_{\text{As}} = 4.27 \times 10^{-2}$ per cent; after the second distillation, 1.52×10^{-2} per cent; after distillation with copper, 2.33×10^{-3} per cent. 36. $K = 603$, $C = 1.83 \times 10^{-2}$ μg .

3. Assignments for Programmed Questioning

1. (b). 2. (d). 3. (c). 4. (e). 5. (a). 6. (b), (d), (g).
 7. (c), (e). 8. (a), (c), (f). 9. (a)—7; (b)—5; (c)—1; (d)—8;
 (e)—2; (f)—6; (g)—3. 10. (a)—5; (b)—7; (c)—6; (d)—1;
 (e)—8; (f)—3; (g)—4.

Chapter XIII

2. Problems

1. 80 per cent. 2. 73.8 per cent. 3. $D_{\text{sol}} = 0.06$, $D_{\text{ext}} = 0.59$. 4. $V_{\text{La}} = 2.4$ ml, $V_{\text{Th}} = 3.6$ ml, $V_{\text{sm}} = 3.2$ ml. 5. 0.62 mg-eq/g. 6. 0.323 g. 7. 0.47 mg-eq/g, total dynamic capacity = 0.801 mg-eq/g. 9. 16.0 per cent. 11. I—18.2 μg , II—72 μg , III—20 μg . 12. 3.58 per cent. 13. $C_{\text{benz}}^{1.7}/C_{\text{w}} = 0.48$; $C = 0.067M$. 14. 2.13×10^{-5} per cent. 15. $1.25 \times 10^{-2}M$. 16. Three-fold. 17. 90 per cent. 18. 99.4 per cent. 19. (3.7 ± 0.4) per cent. 20. 0.071 per cent, 0.049 per cent, 0.064 per cent. 21. 0.83 per cent. 22. First standard— $C_0 = 8.9 \times 10^{-6}$ per cent, $C_{\text{H}} = 3.5 \times 10^{-6}$ per cent, $C_{\text{N}} = 1 \times 10^{-5}$ per cent. After burning-up, $C_{\text{N}} = 1 \times 10^{-5}$ per cent, $C_0 = 7.1 \times 10^{-6}$ per cent. Second standard— $C = 5 \times 10^{-6}$, $C_{\text{H}} = 2.6 \times 10^{-6}$, $C_{\text{N}} = 7.7 \times 10^{-6}$. After burning-up, $C_{\text{N}} = 7.7 \times 10^{-6}$, $C_0 = 3.7 \times 10^{-6}$; 23. 18.0 $\mu\text{g/kg}$.

3. Assignments for Programmed Questioning

1. (b). 2. (d). 3. (c). 4. (a). 5. (b), (e), (f). 6. A—(a), (e), (h); B—3, 4, 7, 8. 7. (a)—6; (b)—9; (c)—4; (d)—1; (e)—7; (f)—3. 8. (a)—3; (b)—2; (c)—4; (d)—1; (e)—5. 9. (a)—3; (b)—6; (c)—5; (d)—4; (e)—2; (f)—1. 10. A—(b), B—3.

Chapter XIV

2. Problems

1. 1.60×10^{-6} gram. 2. 0.225 μg . 3. 4.6×10^{-5} $\mu\text{g/ml}$. 4. 99.2 per cent. 5. 0.111M. 6. 27.0 $\mu\text{g/100 ml}$. 7. 1.35 $\mu\text{g/ml}$. 8. 8.1×10^{-3} per cent. 9. 9.95×10^{-2} per cent. 10. 1.45×10^{18} atoms/cm². 11. 435 gram. 12. $W_{\text{in}} = 8.82 \times 10^{-2}$ ohm⁻¹, $W_{\text{fin}} = 3.82 \times 10^{-2}$ ohm⁻¹. 13. $g_{\text{m}} = 8.27$ grams, $g_{\text{b}} = 4.28$ grams. 14. $C_1 = 1.98$ mmoles/litre, $C_2 = 3.01$ mmoles/litre. 16. $C_{\text{VIV}} = 1.2 \times 10^{-3}$ mole/litre, $C_{\text{VV}} = 4.35 \times 10^{-4}$ mole/litre. 17. The content of glucose is 0.33 g/100 ml, that of fructose, 1.32 g/100 ml. 18. 1.23×10^{-3} per cent. 19. 16.1. 20. CdSe·Cd_{0.04}. 21. CdGeAs₂ × (CdAs)_{0.25}. 22. 81.95 μg . 23. $H^0 = -1.75$ kcal/mole.

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